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PROCEEDINGS OF CONFERENCE ON THE VAPOR-PHASE FINISHING OF COTTON

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February 24, 1967
at
New Orleans, La.

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

FOREWORD

The Southern Utilization Research and Development Division (SURDD) is constantly striving to develop new and improved uses of Southern agricultural products. Among the most important of these endeavors are those in the area of cotton finishing.

A principal purpose of this Conference is to enable SURDD and participants to present uniformly and at one time its information on the vapor-phase finishing of cotton.

These proceedings report the statements presented by the various speakers and give an account of the discussions during the Conference.

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Director
Southern Utilization Research and Development Division

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CONTENTS

Page

Welcome and opening remarks
C. H. Fisher 1

Introductory remarks
G. S. Buck, Jr. 6

Summary of vapor-phase research at the Southern Division
J. D. Guthrie 7

Information basic to the development of vapor-phase durable press processes
H. L. E. Vix, Chairman 11

Crosslinking of cotton with formaldehyde in the vapor phase
N. B. Knoepfler 12

The Vapor-phase crosslinking of preimpregnated cotton fabrics
H. J. Janssen 22

The VP-3 process--summary and conclusions
D. D. Gagliardi 28

National Cotton Council of America's vapor-phase research
Henry Tovey 37

PANEL: INDUSTRY'S INTEREST IN THE VAPOR-PHASE TECHNIQUE FOR COTTON FINISHING
M. E. Heard, Chairman

Comments:

J. W. Weaver 42

C. Tomasino 43

J. W. Pearce 43

Werner Pels 44

Microscopical examination of samples of cotton fabrics given vapor-phase treatments
M. L. Rollins, A. M. Cannizzaro, and I. V. deGruy
(Presented by M. L. Rollins) 49

Durable-press cotton research at the Southern Division
W. A. Reeves 54

Research in the Cotton Mechanical Laboratory
R. A. Rusca 57

Attendance List 67

WELCOME AND OPENING REMARKS

by
C. H. Fisher, Director
Southern Utilization Research and
Development Division

It is my pleasure and privilege--on behalf of the Southern Utilization Research and Development Division (SURDD)--to welcome you to this Conference on vapor-phase finishing of cotton. We consider it a privilege to meet with you, to discuss cotton research, and to display our facilities. Dr. Fred R. Senti, Deputy Administrator, Nutrition Consumer and Industrial Use Research, Agricultural Research Service, USDA, has asked me to extend his greetings and best wishes.

This Conference was arranged in a short time and without the realization that the interest and attendance would be so gratifying. The fact that a conference was quickly and successfully arranged is due to the friendly cooperation and skillful work of many persons both in the Southern Regional Laboratory and other organizations. I wish to thank everyone contributing to this Conference.

For the benefit of those who have limited information about the SURDD and the Agricultural Research Service of USDA, I shall present information on our organization and its objectives, functions, and operations.

The Southern Regional Research Laboratory (SRRL) is one of the four large laboratories of the U. S. Department of Agriculture engaged in agricultural processing and utilization research. It is headquarters for the Southern Utilization Research and Development Division of USDA's Agricultural Research Service. SRRL, with about 471 employees, has almost 90 percent of the facilities of SURDD. The other 10 percent of the facilities of this Division are located in smaller laboratories at Winter Haven and Olustee, Fla., Raleigh, N. C., and Weslaco, Tex.

The objectives of the SURDD are to enrich agriculture by finding new or expanded uses for the principal southern-grown farm crops; to develop new products and processes for industry; to provide consumers with new and better products at lower costs, thereby contributing to improved health, convenience, and comforts; and, in general, to enhance the economy and well-being of the Nation.

We reach these objectives by doing research on the chemical composition, chemistry, processing, and utilization of the principal southern farm crops.

The two principal products of our research are:

First, our research produces information. This new fundamental and scientific information is disseminated in about 250 publications annually. This information is highly valuable to research, education, agriculture, industry, and consumers in most parts of the world. SURDD has published nearly 3,500 papers and about 400 patents.

The two principal requirements of our information program are: (1) The results must be released promptly; and (2) the results must be released in such a manner that all citizens have an equal opportunity to receive and use them.

Second, our research produces new and improved products and processes for industry and consumers. Our research has been responsible for--or has contributed substantially to--about 100 commercialized developments. These have enriched our economy and have facilitated better living for consumers. Examples of our research achievements are:

Major contributions to the development of wash-wear cottons, which are responsible for the sale of more than 1 million bales (500 million pounds) annually of cotton.

Contributions to improved all-cotton durable-press (DP) products.

Nine new machines used in the commercial processing of cotton.

Stretch cotton yarns, fabrics and garments; flame resistant cotton products; improved cotton batting (Cotton Flote).

Improved cottonseed feeds and nutritious cottonseed flour for human consumption.

Frozen orange concentrates developed by our Winter Haven, Fla., Laboratory in cooperation with the Florida Citrus Commission.

Instant sweetpotato flakes.

Partially defatted peanuts.

Several industrial chemicals from turpentine and rosin.

About 99 percent of the funds invested in research and development by SURDD is provided by Congressional appropriation, and about 1 percent is provided by industrial or educational organizations. These are listed below:

Foundation for Cotton Research and Education
Cotton Producers Institute
National Cottonseed Products Association, Inc.
National Cotton Batting Institute
Textile Fibers & By-Products Association
International Lead Zinc Research Organization, Inc.
Canvas Products Association, International
Florida Citrus Commission
North Carolina Agricultural Experiment Station

Earlier supporters of SURDD research include:

Pulp Chemicals Association
National Confectioners' Association

About 92 percent of the research in 1967 is done in the facilities of SURDD, and about 8 percent is done by contractors and grantees. (The proportion of work done by contract and grant decreased from 23 percent in 1964 to about 4 percent in 1966.) Basic research supported by counterpart or P. L. 480 funds is done by grantees in several countries.

Most of the research of this Division is done in cooperation with various educational, industrial, and other research organizations. Official advisers are appointed to provide recommendations and advice about research and approaches that will be expected to give the answers with minimum expenditure of funds and effort.

SURDD is grateful for this and all other valuable cooperation and help.

About 65 percent of the total intramural effort is invested in research on the industrial crops (cotton and naval stores (table 1). The remaining portion of the total effort is concerned with food and feed products. Cotton lint or fiber (60 percent), cottonseed (14 percent), and citrus fruits (9 percent) received most attention.

Table 1. --Southern Utilization Research and Development Division: Program by commodities in 1966[1]

Item	Total man-years[2]	Percent of total effort
	Number	
Industrial (64.9 percent):		
Cotton	316	60.0
Naval stores	25	4.9
Food and feed (35.1 percent):		
Cottonseed	72	13.7
Peanuts	34	6.5
Citrus and other fruits	46	8.7
Vegetables	24	4.6
Sugars and sirups	3	.6
Rice	5	1.0
Total	525	--

[1] Intramural program. Research on sugarcane, tung, and new crops terminated June 1965.

[2] About 60 percent of the total staff is professional or technical.

The Southern Utilization Research and Development Division holds a Cotton Utilization Research Conference (and others) annually to disseminate information promptly about research done during the preceding year[1] SURDD research scientists present papers describing advances in research at various scientific meetings. The research is described also in papers published in various technical journals.

A single free copy of reprints may be obtained by writing to: Southern Utilization Research and Development Division, ARS, U. S. Department of Agriculture, P. O. Box 19687, New Orleans, La. 70119.

The major inventions are described in patents.

Patents on inventions of Department of Agriculture employees, contractors, and grantees, made within the scope of their em-

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[1] Seventh Cotton Utilization Research, New Orleans, La. (ARS 72–63)

employment, are usually assigned to the United States of America as represented by the Secretary of Agriculture. Assigned patents make up the main proportion of Department of Agriculture patents. A license to practice the invention may be obtained from the Department. This type of patent may be identified by the statement of assignment which appears beneath the title and after the inventor's name.

Licenses are granted to any individual showing good faith and willingness to give proper attention to the development. The licenses are currently issued without cost to the licensees, and no royalties, fees, or other charges are made.

Any license issued by the Department of Agriculture on patents assigned to the Secretary is nonexclusive, nonassignable, and revocable.

If a license is desired under an assigned patent, a letter should be addressed to the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, P. O. Box 19687, New Orleans, La. 70119, stating the name, principal place of business of the proposed licensee, together with the name of the person who is authorized to sign on behalf of the licensee. The letter should also set forth the title of the invention and the patent number.

This information can be obtained from a printed copy of the patent or from the abstract as published in the Official Gazette of the U. S. Patent Office.

The Department will prepare the necessary form of license for execution.

Copies of patents may be purchased from the U. S. Patent Office, Washington, D. C. 20231, 50 cents per copy.

For the inhouse work, the inventors (employees of USDA) may obtain foreign patents describing their inventions and the foreign rights with some limitations, after receiving permission for doing this from the USDA.

A standard clause or paragraph of the contract document states that the U. S. Government will have both the domestic and foreign patent rights to inventions made under the terms of USDA contracts.

With the exception that the inventions (both domestic and foreign) made by employees of the contractor remain the property of the Federal Government, the procedures and requirements are the same. That is, all the information worthy of publication is published. The inventions are patented in the United States and assigned to the Secretary of Agriculture for the free use of U. S. citizens.

The above-made statement applies only to research done by the contractor as a part of his contract for the U. S. Department of Agriculture. Research that might have been done by the contractor with his own funds--and outside of the contract requirements--is entirely another matter. SURDD, in working with its contractors, makes no effort to learn about research activities of the contractor outside the terms of the contract.

The first research in SURDD involving vapor-phase crosslinking of cotton was initiated about 1960 by John D. Guthrie. The results of this research were presented or published as follows:

A. Presented at the May 1961 Cotton Utilization Research Conference in New Orleans.
B. Guthrie, J. D. Imparting wrinkle resistance to cotton fabrics with vapor from HCL-paraformaldehyde. Amer. Dyestuff Rptr. 51, 507-512. 1962.
C. Gonzales, E. J. and Guthrie, J. D. The crosslinking of cotton cellulose with gaseous formaldehyde in the presence of various compounds. Amer. Dyestuff Rptr. 54, 735, 765-768. 1965.
D. Guthrie, J. D. Process for treating cellulosic textiles with formaldehyde in the vapor form. (U. S. Patent Office, Off. Gaz. 807:983. 1964.)
E. Guthrie, J. D. Process for treating cellulosic textiles with formaldehyde in the vapor form. (U. S. Patent Office, Off. Gaz. 813:1380. 1965.)

J. David Reid and his colleagues in SRRL also have investigated vapor-phase crosslinking treatments. Results have been reported as follows:

A. On March 24, 1962, a paper was presented before the Northern Piedmont Section of AATCC at Raleigh, N. C., and later published as follows:

   Arceneaux, R. L., Fujimoto, R. A., Reid, J. D., and Reinhardt, R. M. Crosslinking of cotton with gaseous formaldehyde. Amer. Dyestuff Rptr. 51: P559-P566. 1962.

B. Reinhardt, R. M. and coworkers. Process for crosslinking cellulosic textile and paper materials with gaseous formaldehyde. (U. S. Patent Office, Off. Gaz. 829: 282. 1966.)
C. Preprint available at the Feb. 24, 1967, Conference: Reinhardt, R. M., Bruno, J. S., Fujimoto, R. A., and Reid, J. D. Gaseous acid catalysis in the durable press finishing of cotton.

C. J. Conner published a brief investigation of vapor-phase crosslinking of silicone-treated cotton entitled "Vapor Phase Reaction of Formaldehyde with Silicone Treated Cotton," Amer. Dyestuff Rptr. 54: 618. 1965.

J. D. Guthrie's talk this morning will review in greater detail the research in the SRRL on vapor-phase treatments.

The Gagliardi Research Corporation conducted research for SURDD on the vapor-phase treatments of cotton from April 1964 to October 1966.

The results of this work, which has created much interest, have been released promptly.

The final report of the Gagliardi Research Corporation includes a summary of the research data and, in addition, covers work for the final reporting period. This report was received by our Division on February 13, 1967. The unpublished work of the Gagliardi Research Corporation, done under contract for SURDD, will be summarized at this Conference by Mr. Knoepfler, Mr. Janssen, and Mr. Gagliardi. A written summary of the unpublished work on durable press as carried out under this contract is being prepared.

Pending patent applications covering vapor phase treatments are:

Reinhardt, R. M., and others. Process for producing wrinkle resistant cellulosic textile materials by treatment with formaldehyde.
Reinhardt, R. M., and others. Process for producing wrinkle resistant cellulosic textile materials by gaseous catalysts.
Gagliardi, Donald. Vapor phase treatment of fabrics. (Describes processes invented during research under contract for USDA).

Information resulting from contract research by the Gagliardi Research Corporation has been reported as follows:

A. In 1965 at the Cotton Chemical Finishing Conference (National Cotton Council) the paper entitled "Vapor phase reactions on cotton" was presented and later published as "Vapor phase reactions on cotton. Part I: General considerations and partial results". Textile Res. J. 36: 168-188. 1966.
B. A paper entitled "Vapor phase formation of resins and polymers in cotton fabrics" was presented at the Fiber Society meeting in Atlanta, Ga., in May 1965.
C. A lecture was given at the CATCC (Canadian) on February 18, 1966, in Montreal, Canada, relating to a literature search on the organic chemistry, catalysts, and practical applications of grafting with improved strength and abrasion which contained some of the information obtained from the contract research.
D. In March 1966 the paper entitled "Vapor phase permanent press" was presented at the meeting of the Textile Research Institute.
E. Preprints of the paper mentioned in B (above) were widely distributed in March 1966.
F. In April 1966, the paper "Vapor phase grafting and its relation to perman-

ent press" was presented and published in Proceedings of the Sixth Cotton Utilization Research Conference, U. S. Dept. Agr., Agr. Res. Serv., ARS 72-52, pp. 37-38. 1966.

G. Gagliardi, D. D. and coworkers. Vapor phase reactions on cotton, Part II, Textile Res. J. (In press).
H. In 1967 Proceedings of Conference on the Vapor-Phase Finishing of Cotton--this issue.

Pending are the patent application by D. Donald Gagliardi entitled "Vapor Phase Treatment of Fabrics" and a talk scheduled before the Textile Finishing Conference in Switzerland, March 1967.

The vapor-phase research by SURDD and by the Gagliardi Research Corporation has created wide and strong interest.[2] We hope that this interest is fully justified and that vapor-phase methods will be used on a commercial scale to benefit cotton and to provide the consumer with better products.

We are aware that the research by SURDD, and by contract is incomplete and that more work and development are needed. This is usually the case even when the initial research is promising and attractive.

Additional research and development needed include:

A. Development of more information on parameters such as the effects of temperature, time, pressure, catalysts, and moisture content of the cotton.
B. Effect of the treatment on colors.
C. Reduction of multiple step processing (e. g., grafting and crosslinking) to a single step process.
D. Development of suitable equipment for large-scale processing.
E. Development of improved vapor circulation might be helpful, especially for several layers of fabrics.
F. Efficient method suitable for removing unreacted vapors at the end of the treatment.

The vapor-phase techniques, depending upon the particular method chosen, may have advantages of:

A. The products having a high level of chlorine resistance when nitrogen compounds are not used.
B. Low reaction temperatures resulting in enhanced mechanical properties and reduced operating costs.
C. Reaction essentially complete during the period of vapor exposure and curing ovens that do not provide any significant increase in yield of bound resin.
D. Avoid handling of liquids, such as dipping, padding, and drying.
E. Suitability for treating of delicate fabrics such as laces; also knit goods and molded fabrics.
F. Preliminary investigations indicating that the distribution of crosslinks may be unusually uniform.

As stated above, more research and development are needed. It has been indicated, however, that industrial firms are engaged--or plan to become engaged--in research and development of the vapor phase treatments for making durable-press products. This suggests that currently there is no need for SURDD to further sponsor research and development in this area.

The Division has a relatively large research effort invested in the development of improved durable-press products. The vapor-phase treatment approach is only one part of the total effort, which amounts to about 50 professional man-years per year.

In September 1964, SURDD intensified its research in the area of durable-press. The results of this intensified and coordinated effort have been gratifying. About 40 research papers and patents describing our work on durable-press have been published. Several new methods for improving abrasion resistance of all-cotton durable-press products have been developed. These are:

(1) Use of improved yarn and fabric structure.
(2) Application of tough polymers, e. g., polypropylene and selected acrylates.
(3) Application of polymers (e. g., selected silicones, urethanes, and polyethers) followed by polymer crosslinkage.

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[2] The following talk is scheduled for presentation at the May 4–5, 1967, meeting of The Fiber Society, Asheville, N.C.: "A Preliminary Study of the Vapor Phase Encapsulation of Cotton Fabrics" by J.C. Goswami, B. Rugg, W. Brenner, M. Prince, and W.H. Kapper, New York University, New York, N.Y.

(4) Preferential crosslinkage, that is, crosslinkage in selected regions of the fabric. (Treated corduroys are an example).
(5) Slack mercerization, hydroxyethylation, and similar pretreatments.
(6) Treatments that take advantage of the helpful effect of the swelling of cotton fibers. (One of these is called "Polyset.")
(7) Use of blends of untreated cotton with treated cotton.
(8) Attachment of long side chains to the surface of cotton fibers.

The first three advances listed above are already being used industrially. The other five are being evaluated by the textile industry.

The new carbamate finishes developed by SURDD scientists are used in the production of about 80 percent of all-white durable-press products.

Much of the successful research referred to above has been conducted in cooperation with the National Cotton Council and with several other organizations. We are grateful to them, of course, for their valuable help.

It is not yet clear to scientists in SURDD as to which of these individual approaches may be combined advantageously with others. Presumably, the approach of having improved yarn and fabric structures will apply to all other approaches for improving the abrasion resistance of the finished product. Perhaps some of the other approaches will be found additive, too.

In any event, we feel that much progress has been made in this important area of research. This progress over a broad front, particularly when combined with advances made by other organizations, causes us to have considerable optimism about the future of cotton in durable-press and other products.

[NOTE: Although not discussed at the Conference, SURDD initiated support of a contract project involving vapor-phase treatments for cotton at New York University on July 19, 1966. The title of the project is "Investigation of polymer encapsulation of cotton fibers to provide new and useful textile products."}

INTRODUCTORY REMARKS

by

George S. Buck, Jr.
National Cotton Council of America
Memphis, Tenn.

This Conference is an example of the type of activity which has been going on for many years through the work of the Southern Utilization Research and Development Division, but which many of us in industry haven't recognized thoroughly enough; that is, the Division, over the years, has reported its progress to industry at early stages through special meetings, special publications and other means. In general the Division has used the finest spirit of cooperation to get its developments into the hands of industry at early stages so that industry can make its own application of findings of the scientists here.

I think a real tribute is due this organization, which has worked in this way for so many years. I think this meeting is a fine example of the regard which industry generally has come to have for this Division.

I'd like to compliment Dr. Fisher and his staff for sponsoring this meeting, on the very timely development at an early stage of a new and promising subject. Another example of the fine cooperation of the Division was listing the Cotton Council as a cosponsor of this meeting. We hope, in the years ahead, to have a chance to work even more closely with the Southern Regional Research Laboratory.

As some of you know, cotton producers themselves have been supporting research through Cotton Producers Institute. Starting this year, a new program is to be set up under the Research and Promotion Act which was passed by the Congress in 1966, expanding this private research and promotion effort.

We hope, in that effort, to cooperate and work just as closely with the Southern Utilization Research and Development Division (SURDD) as we have in the past; we hope to emulate their excellent example of getting work before the industry at early stages where it can be taken up and applied.

Now, the subject today, "Vapor-Phase Finishing of Cotton for Durable Press and Other Uses," is a relatively new one and that's the main reason we are all here, to hear about the progress that has been made.

The Southern Regional Research Laboratory has pioneered in this area, both in work here and work which the Division has sponsored. We ourselves, in the Cotton Council, have had a little part in this type of research at Stanford Research Institute, at Bjorksten Research Laboratories, and more recently at Gagliardi Research Corporation.

At this point, so far as we are concerned, we can't say what the significance of vapor phase finishing may be. Some aspects of it look very promising.

The process has the potential for both economy and versatility. It can be applied to products that aren't amenable to the ordinary finishing techniques. But, this is essentially a development at an early stage.

I think it would be difficult, at least for us, to project the ultimate commercial significance of vapor-phase finishing for durable press or for some of the other possibilities it has.

I think this is the time to take a good look at vapor-phase finishing, to see what it may mean for you, your firms, and your customers. If you are intrigued enough, you may want to pursue it in your own laboratories and in your own plants and see what you can make of it.

Now, like the rest of you, I want to know more about this new process and this new potential, so I'll turn the meeting back to Dr. Wojcik and join you in listening to what's going to follow.

SUMMARY OF VAPOR-PHASE RESEARCH AT THE SOUTHERN DIVISION

by
John D. Guthrie
Cotton Chemical Reactions Laboratory
Southern Utilization Research and Development Division

Before summarizing the vapor-phase research in this Division, it seems appropriate to put the subject into proper perspective by generalizing a bit about it. There is nothing particularly new or unusual about applying gases to cotton, although this is not done much commercially, From a research standpoint, vapor-phase treatments are only another way of applying chemicals to cotton comparable to the pad-dry-cure processes, boiling cotton in solutions, and the like. Acid aging of prints is an example of a vapor-phase process that has been with us for a long time. A vapor-phase process of continued interest from a research standpoint is the oxidation of cotton with nitrogen dioxide (14). This produces a product that was tried in surgical sponges that dissolve if left in the patient.

The early work of Musser (12), who reacted cotton with gaseous butadiene monoxide in the presence of sodium hydroxide, had a considerable influence on the initiation of vapor-phase work in the SURDD. This work was called to our attention by the late Raphael E. Rupp, who was one of our advisers. A research proposal, originally submitted by the late Lucien Greathouse, also influenced the course of our vapor-phase work.

Vapor-phase applications to cotton may be put into two broad classes as follows:

Class 1. Processes in which all the reagents and added catalysts are applied in vapor form.

Class 2. Processes in which one or more of the reagents and catalysts are applied in vapor form, the others being applied from solution.

Those processes that fall into class 1 have obvious advantages from the standpoint of simplicity, economy, and effect on the cotton. The class 2 is especially true when application is made to raw stock or to sliver, because the product is not matted or compacted by the process. However, only a limited number of volatile reagents that react with cotton are available, so considerable research has been done with processes of class 2.

The first published vapor-phase application to cellulose of SURDD appears to be that of Hamalainen and Reid (7), which appeared in May 1949. Water-activated linters were pretreated with an ether solution of perchloric acid and then exposed to gaseous ketene at about 100° C. A product containing 22.8 percent acetyl was obtained. The authors state that this process corresponded to treatment with a concentrated ether solution of ketene, rather than reaction with gaseous ketene. It must be pointed out, however, that in most vapor-phase applications to cotton, the reagents probably first dissolve in the water or other liquid present in the cotton, and that the actual reaction occurs in the resulting solution.

The first publication from SURDD that deals exclusively with a vapor-phase treatment is that of Drake, Reeves, and Guthrie (4). Ethelenimine in gaseous form was reacted with cotton sliver in a small vacuum oven. The oven was provided with an addition tube leading to a small beaker in the bottom of the oven. The oven was filled with cotton sliver, heated to about 100° C., evacuated to 10 to 20 mm. of mercury, and the ethylenimine added dropwise. The ethylenimine volatilized uniformly through the cotton and polymerized in and on the cotton fibers. The treated cotton was converted into yarn and fabric without difficulty. The fabric dyed uniformly with an acid wool dye. Aside from changed dyeing characteristics, no outstanding property was noted for the ethylenimine-treated cotton. This vapor-phase treatment was also found useful for increasing the anion-exchange capacity of aminoethylated cotton (3). This interest in ethylenimine led to the production of tris-(1-aziridinyl) phosphine oxide, a useful flame-retardant for cotton.

A vapor-phase method for polymerizing acrylonitrile in and on the fibers of cotton yarn has been described by Haydel and others of our Engineering and Development Laboratory (8). The yarn was wetted with a dilute solution of potassium persulfate and exposed at 80° C. to the vapor of acrylonitrile. The polyacrylonitrile that formed was firmly attached to the cotton fibers. The product had excellent rot resistance and good resistance to flat abrasion.

Cotton treated with solutions of $Zn(BF_4)_2$ has been exposed to the vapor from the racemic mixture of the d, 1-isomers of butadiene diepoxide (9). Weight gains were observed in some cases, but no significant changes in fabric properties were noted. In related experiments (10), it was observed that exposure of dried cotton to BF_3 gas at room temperature resulted in a gain of weight, indicating that the the BF_3 formed a complex with the cellulose.

A process invented at SURDD (13) that makes use of ammonia gas to fix THPC--N-methylol flame retardants in cotton is of special interest, because it may be the only vapor-phase process developed here that is widely used commercially. In this process, and its modifications, the THPC--N-methylol solution is padded on the fabric and fixed by exposure to ammonia gas, rather than by heat curing. The fixation is then completed by passing the fabric through aqueous ammoium hydroxide solution. This process has the advantage of minimizing the crosslinking of the cellulose that is caused by curing with heat. This results in less loss of strength. The ammonia-cure process produces fabrics having softer hand and less stiffness than the heat-cure processes.

Major interest in the field of vapor-phase treatments for cotton has been recently centered on formaldehyde. Formaldehyde has properties that make it very attractive for vapor-phase applications. It is a gas under all ordinary conditions and reacts readily with cotton in the presence of acidic catalysts to impart wash-wear properties by crosslinking the cellulose. Furthermore, it is not expensive. There are at least two volatile catalysts that may be applied with it, namely, hydrogen chloride and formic acid. Since these may be applied simultaneously with the formaldehyde vapor, treatments may be made by a single step, class 1 process.

A convenient vapor-phase method for treating cotton in the form of yarn, fabric, or completed garments was described in 1962 (6). The source of the formaldehyde vapor and hydrogen chloride used in this method was powdered paraformaldehyde which had been exposed to the vapor from concentrated hydrochloric acid for several days. This material was placed in the bottom of a large polyethylene container provided with a paddle-wheel stirrer to mix the vapor. The yarn, fabric, or carefully ironed garment was hung in the container, which was then closed. After 20 to 30 hours at room temperature (about 25° C.), with continuous stirring of the vapor, the materials were removed. They were washed to remove adsorbed formaldehyde and HC 1, or they were hung in air for several days to accomplish this. Good wash-wear properties were imparted by this process. Wrinkle recovery angles, wet or dry, of 250° to 270° W+ F were obtained at combined formaldehyde content of about 0. 1 percent. This is much less than required for comparable recovery angles produced by other formaldehyde methods. Wash-wear ratings of about four were obtained at combined formaldehyde contents of 0. 20 to 0. 25 percent. At formaldehyde contents higher than this, tensile and tear-strength losses became significant in limiting the usefulness of most of the materials processed by the method. Fabrics treated by the process did not lose significantly in formaldehyde content on repeated laundering, but the wash-wear ratings fell from four to about three after about ten home-type launderings. It may be noted that the treatment time in this process was about 24 hours, which most people consider far too slow.

This problem of speeding up the vapor-phase treatment with formaldehyde was investigated by the late Richard Arceneaux, and coworkers (1). By increasing the formaldehyde concentration, the amount of HC1 catalyst and the temperature and by using more sophisticated equipment, these workers found that they could obtain favorable results with a processing time of 1 hour or less.

Vapor-phase formaldehyde treatments have been used to attach many different compounds to cotton. Gonzales and Guthrie (5) have applied various compounds having active hydrogens to cotton, followed by exposure to the vapor from HC1-paraformaldehyde. The formaldehyde reacted with the cellulose and also with the added compound to attach it to the cellulose. The compounds included acids, amides, polyamides, esters, dyes, and certain hydroxy compounds.

The vapor-phase formaldehyde process has also been used to impart wash-wear properties to fabric treated with the so-called silicone alloy of Conner (2). A wash-wear fabric having excellent water repellency was produced.

As to the possible future of vapor-phase formaldehyde processes, I believe that if cotton fabrics made by the method of Murphy, Margavio, and Welch (11) were readily available, there would be a good prospect of making products of commercial interest. In this process of Murphy and coworkers, yarn is slack mercerized and then restretched. Fabrics woven from such yarns show little loss in strength on crosslinking. This should permit the introduction of higher amounts of combined formaldehyde without excessive strength loss and make possible the production of shirts and other garments with excellent wash-wear properties.

Another item that is needed in the development of wash-wear processes based on formaldehyde is a thorough physical-chemical investigation of the system: Formaldehyde, water, HC1, cellulose. Such an investigation would be admittedly very difficult and expensive, but major producers of formaldehyde should have self-interest in financing such such an investigation.

LITERATURE CITED

(1) Arceneaux, R. L., Fujimoto, R. A., Reid, J. D., and Reinhardt, R. M. 1962. Crosslinking of cotton with gaseous formaldehyde. Amer. Dyestuff Rptr. 51: P559-566.

(2) Conner, C. J. 1965. Vapor phase reaction of formaldehyde with silicone treated cotton. Amer. Dyestuff Rptr. 54: 618.

(3) Drake, G. L., Jr., and Guthrie, J. D. 1953. Further aminized amino alkylated cellulose by reacting with ethylenimine. (U. S. Patent No. 2, 656, 241) U. S. Patent Office, Off. Gaz. 675: 761.

(4) Drake, G. L., Jr., Reeves, W. A., and Guthrie, J. D. 1953. Ethylenimine-treated cotton. Textile Res. J. 23: 639-641.

(5) Gonzales, E.J., and Guthrie, J. 1965. The crosslinking of cotton cellulose with gaseous formaldehyde in the presence of various compounds. Amer. Dyestuff Rptr. 54: 735, 765-768.

(6) Guthrie, J.D. 1962. Imparting wrinkle resistance to cotton fabrics with vapor from HCl-paraformaldehyde. Amer. Dyestuff Rptr. 51: 507-512.

(7) Hamalainen, C., and Reid, J.D. 1949. Partial acetylation of cotton cellulose by ketene. Indus. Eng. Chem. 41: 1018-1021.

(8) Haydel, C.H., Janssen, H.J., Seal, J.F., Vix, H.L.E., and Gastrock, E.A. 1957. Vapor phase method for preparation of polyacrylonitrile coated cotton yarn and physical properties of the product. Textile Res. J. 27: 975-982.

(9) McKelvey, J.B., Benerito, R.R., and Berni, R.J. 1965. Cellulose-d,1-butadiene diepoxide reactions catalyzed by Lewis acids. J. Appl. Polymer Sci. 9: 191-205.

(10) McKelvey, J.B., Webre, B.G., and Benerito, R.R. 1960. Reaction of cotton cellulose with epoxides in the presence of acid catalysts. Amer. Dyestuff Rptr. 49: 804-809.

(11) Murphy, A.L., Margavio, M.F., and Welch, C.M. 1964. A method of preventing strength losses during wash-wear finishing of cotton fabric. Amer. Dyestuff Rptr. 53: 42-43.

(12) Musser, D.M. 1948. Cellulose ethers of 3,4 epoxy 1-butene and their oxidation products. (U.S. Patent No. 2,455,083) U.S. Patent Office, Off. Gaz. 616: 1333.

(13) Reeves, W.A., and Guthrie, J.D. 1956. Ammonia insolubilized methylol-phosphorus polymers and cellulosic materials impregnated therewith. (U.S. Patent No. 2,455,083) U.S. Patent Office, Off. Gaz. 712: 788.

(14) Yackel, E.C., and Kenyon, W.O. 1942. The oxidation of cellulose by nitrogen dioxide. J. Amer. Chem. Soc. 64: 121-127.

DISCUSSION

Question: You mentioned that your favorite range was 0.20 to 0.25 percent. Could you comment a little bit more on that?

Dr. Guthrie: Actually, what I was trying to do at the time was to arrive at the highest formaldehyde content you could get, say, in a shirt, without having someone who was putting on a pullover sweater with his shirt on having his elbows stick out through the shirt.

When you went much higher than 0.25, you began to experience that phenomena. So that was about as far as you could go and get increase recovery angles up to about 0.28 percent formaldehyde.

I might mention that I had swatches of fabric in with the shirts and I would take a piece of the fabric out, make a hand-crumpling test, a crumpling test in water, and a tear test with the hand to see if it were tendered enough, then when it got to the right point, I could take the shirt out and consider it completed.

Question: Can you tell us something about the history of the shirts? How was the fabric prepared? Whose shirts were they? What state were they in? Did they have softeners on them?

Dr. Guthrie: Well, the shirts were bought at a department store. They were regular all-cotton shirts. Even then it was a little difficult to find a white all-cotton shirt that didn't already have a wash-wear treatment on it. They were commercial cotton shirts, bought at the store, very carefully ironed after they were taken out of the package, and then hung in the barrel. They weren't special-made. If they had been, of course, better results would have been obtained, I am quite sure.

Question: I'm not familiar with the work you referred to by Murphy, Margavio, and Welch, but do you have an explanation why the premercerization gives a product which is not tenderized by the formaldehyde treatment?

Dr. Guthrie: Well, there have been explanations for it. The one I like best is that the cotton is first mercerized slack and then restretched, and I think what happens is that the fibrils of the cellulose are oriented better. I would say that any kinks in them were taken out so that they were crosslinked. It's a matter of orienting the microscopic or the substructure of the cotton so it's in position to bear loads better after crosslinking. I think there are other explanations, but that's the one I like.

INFORMATION BASIC TO THE DEVELOPMENT OF VAPOR-PHASE DURABLE PRESS PROCESSES

by
H. L. E. Vix, Chairman

INTRODUCTION

Now that Dr. Guthrie has set the stage for us to discuss some particular findings with respect to the vapor-phase treatment of cotton, we will focus our attention to that part of the program dealing specifically with the research of the Gagliardi Research Corporation under contract with the Southern Utilization Research Development Division (SURDD) from April 1964 to November 1966.

The research plan covered in this contract resulted from ideas, proposals, and research of several scientists at the SURRD. This particular contract covered basic investigations of vapor-phase reactions of cotton cellulose designed to explore a wide variety of gaseous chemical reagents, with particular emphasis on the initiation or acceleration of such reactions to provide information as a basis for the development of improved cotton chemical processing techniques and new and improved cotton products.

This particular research contract covered five major areas of vapor-phase reactions:

1. Esterification
2. Etherification
3. In situ polymerization
4. Graft polymerization
5. Crosslinking

The objective of the work was investigation of vapor-phase or gaseous reagents and catalyst systems for their effectiveness in reactions with cotton to yield products having new and useful properties from each of the above types of reactions or combinations thereof.

Significant information was developed in each of these five areas. Of particular interest was the development of durable-press characteristics through vapor-phase crosslinking and graft-polymerization techniques.

As a result of several previous presentations by Mr. Gagliardi reporting the progress being made under this contract, much interest has developed in the feasibility of utilizing vapor-phase reactions as a means of producing durable press type products.

Of the three previous presentations made by Gagliardi Research Corporation, technical reprints are available of one, and either preprint or proceedings reproductions are available of the other two.

This workshop has been arranged in the interest of conveying complete data to those interested in the vapor-phase technology as developed under this USDA contract with Gagliardi Research Corporation.

Nestor B. Knoepfler and Hermann J. Janssen will present some of the basic research of this contract which has not been published.

Much of the data, which will be presented, has been used in reaching conclusions reported in some of the previous presentations and in the published material resulting from the contract.

Donald Gagliardi will present a general summary of the state of the art of vapor-phase durable press research, and its commercial potentialities.

We would appreciate it if you will hold questions concerning any of the presentations for this session until all three presentations have been made.

CROSSLINKING OF COTTON WITH FORMALDEHYDE IN THE VAPOR PHASE

(Presented by N. B. Knoepfler)
Engineering and Development Laboratory
Southern Utilization Research and Development Division

For almost 60 years, the reaction of formaldehyde with cellulose has been known and studied. Roff (28) in a review of the subject to 1956 lists 74 references.

In the last 10 years, the application of formaldehyde to cotton has assumed greater importance because of the consumer demand for wash-wear properties including wrinkle resistance, and, subsequently, durable press characteristics.

Wide commercial use of formaldehyde in textile finishing has been deterred because of technical difficulties in the application of the chemical and deficiencies in the products, such as excessive loss of strength when adequate wash-wear ratings were achieved (2). There are, of course, outstanding advantages to be gained if an acceptable finishing technique could be developed that would overcome the deficiencies. Among the advantages are the low cost of the formaldehyde, durability of the crosslink during use and laundering (16, 17, 27), and chlorine resistance (2, 26).

Methods of applying formaldehyde include the conventional pad-dry-cure (1), water or calcium chloride solutions (3, 25), aqueous formaldehyde-formic acid or HCl (13, 21, 23, 26), Form D-Form W treatment (4), and in the gaseous or vapor-phase (2, 14, 27).

Reeves and coworkers (25, 26) recognized that the degree of swelling of the fibers at the time crosslinking with formaldehyde was accomplished had a great bearing upon the properties of the products. Guthrie (15) showed that the concentration of the formaldehyde had a profound effect upon the amount of combined formaldehyde required to change the crease recovery and other physical properties of cotton fabric.

Between 1954 and 1956, Greathouse (11), Fisher and Gastrock (9), and Janssen and Vix (20, 31) recognized the importance of vapor-phase reactions in the chemical modifications of cotton and proposed that research into such reactions be made.

Vapor-phase chemical treatment of cotton offers great versatility. Cyanoethylation[1] (5) and polyacrylonitrile-coated cotton (19, 22) are examples of vapor-phase treatment to achieve heat and rot resistance. Enhanced dye receptivity can be attained by ethylenimine vapor treatment of cotton (7). Flame retardancy can be conferred upon cotton impregnated with certain polymers by exposure to ammonia vapor (8, 24). Wash-wear properties can be gotten by exposing cotton to formaldehyde vapors (2, 14) and these properties supplemented with water repellency by the use of silicone (6).

Because of the above, reactions had not been systematically explored in depth and research into vapor-phase reactions for cotton was undertaken in 1964 in the framework of the USDA's contract research program with Gagliardi Research Corporation as the contractor.

The research was based upon the original research proposal of Greathouse (11), which had been expanded to incorporate the ideas suggested by Janssen, Vix, Fisher, and Gastrock and upon a proposed program of research selected from the prospectus by Gagliardi.

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[1] Steen, G.J., and Janssen, H.J. 1958. The vapor phase cyanoethylation of cotton. [Manuscript]

This report will deal only with the crosslinking of cotton with formaldehyde and the development of a suitable catalyst system to achieve durable-press characteristics with improved resistance to abrasion damage. This was only one phase of the research envisioned and carried out under the above contract.

Table 1. --Weight gain produced from various sources from 2 day's exposures at 21° C. [10 g. contained formaldehyde; 25 ml. concentration Hcl.]

Formaldehyde source	Initial weight gain
	Percent
91-pct. paraformaldehyde	-0.3
40-pct. butyl formcel	.1
55-pct. methyl formcel	.6
37-pct. aqueous formaldehyde	2.9

Research. -- Although considerable information was available on the crosslinking of cellulose with formaldehyde, and particularly upon the effect of swelling of the fibers at the time this research was initiated, little was known about the influence of the state of the formaldehyde at the time of crosslinking, or the effect of the catalyst system used. The known behavior of formaldehyde in various solvents indicates that the concentration and the temperature might be expected to influence the length and the amount or number of the introduced crosslinks, and thus affect the properties of the products. These effects could be noted in crease recovery, strength, and other fabric properties (14). Because the vapor pressure of the formaldehyde varies widely with solvent and the formaldehyde is known to form a variety of azeotropes with water and alcohols (32), a series of tests were made to ascertain the efficacy of several sources of formaldehyde as donors for vapor-phase reactions. From table 1 it can be observed that the aqueous and methyl formcel solutions gave the highest weight gains on cotton under the conditions used. This could be anticipated based upon the partial pressure exerted by the formaldehyde in the different forms which ranged from about 2 mm. for the paraformaldehyde up to possible 250mm. for the aqueous formaldehyde (32). Guthrie's work (14) illustrated in table 2 compares products made by two different vapor-phase paraformaldehyde treatments (2, 14). The concentration of formaldehyde in the vapor affects the amount of combined formaldehyde required to produce a given effect upon the physical properties of the products. Guthrie speculated that higher concentrations of formaldehyde might be expected to favor the introduction of more dimeric and trimeric crosslinks than would be obtained at lower concentrations, and that higher concentrations would be less effective per unit of formaldehyde than lower concentrations (14, 18). Table 2 also shows, for example, at 25° C. and a partial pressure of 2mm. a weight gain of formaldehyde of 0.19 percent gave a crease angle of 273. This can be contrasted with a crease angle of 272 attained at 80° C. and a partial pressure greater

Table 2. --Effect of the partial pressure on the amount of combined formaldehyde required to produce a given dry crease recovery in vapor-phase treatments

Method of treatment	Reference	Temperature	Partial pressure CH_2O	CH_2O content of fabric	Dry crease recovery angle (W+F)	Breaking strength retained (warp)
		°C.	MM.	Percent	Degree	Percent
Guthrie	14	25	2	0.19	273	59
	14	25	2	.28	288	47
	14	25	2	.44	302	49
	14	25	2	.51	298	47
Arceneaux	2	20	150 [1]	.50	256	64
	2	30	150 [1]	.15	227	68
	2	30	150 [1]	.23	244	60
	2	30	150 [1]	.34	274	56
	2	30	150 [1]	.54	294	52
	2	50	150 [1]	.50	276	55
	2	80	150 [1]	.38	272	51

[1] Approximation based on method of treatment described in reference 32.

than 150 mm. with double the weight gain. Other researchers have recognized that only a small amount of formaldehyde is needed to produce a profound effect on the physical properties of cotton (10, 12), and that improvement in crease recovery angle was not necessarily related to weight gain. Methods of measuring the effectiveness of crosslinking achieved by various processes have been reported (29, 30). For this reason the methanolic formaldehyde solution was chosen over the aqueous system for further research. It was recognized that the catalyst also would have a significant effect upon the weight gain as well as the physical properties of the products. Table 3 shows data obtained for samples of fabric that had been preimpregnated with aqueous solutions of various salts and then dried for 5 minutes at 220° F. The weight gain was exceedingly small even after 14 days' exposure to the vapors from paraformaldehyde. These results can be interpreted as indicating (a) insufficient formaldehyde or (b) deficient catalysts. The above procedure was rerun for an exposure time of 7 days and a half of the samples were cured for 10 minutes at 300° following exposure. Weight gains for both halves were still small. The cured samples, however, demonstrated an improvement in crease resistance and immunization to dyeing with Fastusol Blue LBRRA (a direct blue cotton dye) while the uncured portion of samples demonstrated neither crease resistance nor dye resistance. Table 4 shows the results.

Table 3. --Weight gain of samples of cotton fabrics impregnated with acidic catalysts (1 percent) after exposure to the vapors of 91 percent paraformaldehyde at 21° C. for times up to 14 days

Catalyst applied	Exposure time	Weight gain Initial	Weight gain fixed
	Days	Percent	Percent
$MgCl_2 \cdot 6H_2O$	1	0.4	-0.1
	7	.8	-.1
	14	.8	-.2
$Zn(BF_4)_2 \cdot 7H_2O$	1	.1	-.1
	7	1.2	.1
	14	1.1	
$CuCl_2 \cdot 2H_2O$	1	.2	.0
	7	.8	.2
	14	.7	.4
$Zn(NO_3)_2 \cdot 6H_2O$	1	.1	-.1
	7	.7	-.1
	14	.8	.3
NH_4Cl	1	.3	-.4
	7	.5	-.4
	14	.6	.2

The effects of temperature upon the reaction of formaldehyde from paraformaldehyde with cotton fabrics impregnated with metal salt (latent acid) catalysts are shown in table 5. For these experiments an exposure time of 24 hours was used. At 80° C. both ammonium chloride and cupric chloride gave high crease resistance even though weight gains were so small they were difficult to measure. Substituting methyl formcel for the paraformaldehyde gave the results shown in table 6. One significant difference between formaldehyde from paraformaldehyde and formaldehyde from methyl formcel could be observed in the weight gain of the cotton fabric after exposure. In this case also best results were again obtained with ammonium chloride and cupric chloride while magnesium chloride was ineffective. Table 7 shows the results obtained when cotton fabric, which had been padded

Table 4. --Effect of exposure of cotton fabrics impregnated with acidic catalyst (1 percent) to 91-percent paraformaldehyde vapors at 21° C. for periods up to 7 days upon dyeing characteristics and crease recovery angles

Catalyst	Exposure	Dye test [1] Vapor only	Dye test [1] Plus cure	Crease recovery angle-warp Vapor only	Crease recovery angle-warp Plus cure
	Days				
$MgCl_2 \cdot 6H_2O$	1	-	-	85	88
	7	-	+	85	131
$Zn(BF_4)_2 \cdot 7H_2O$	1	-	-	85	89
	7	-	+	85	101
$CuCl_2 \cdot 2H_2O$	1	-	-	85	90
	7	-	+	85	135
$Zn(NO_3)_2 \cdot 6H_2O$	1	-	-	85	87
	7	-	+	85	135
NH_4Cl	1	-	-	85	90
	7	-	+	85	133

[1] (–) No immunization; (+) immunization.

Table 5. --Effect of temperature upon weight gain and crease recovery angle for cotton fabrics impregnated with acidic catalyst (1 percent) and exposed for 24 hours to paraformaldehyde vapor

Catalyst	Temperature	Weight gain Initial	Weight gain Fixed	Crease-recovery angle-warp
	° C.	Percent	Percent	
$MgCl_2 \cdot 6H_2O$	50	-0.2	-0.9	76
	80	.4	.0	114
$Zn(BF_4)_2 \cdot 7H_2O$	50	-.6	-.7	76
	80	.0	.0	110
$CuCl_2 \cdot 2H_2O$	50	-.2	-.7	72
	80	.2	-.2	142
$Zn(NO_3)_2 \cdot 6H_2O$	50	-.4	-.6	79
	80	.2	-.2	118
NH_4Cl	50	-.2	-.7	134
	80	-.5	-.4	153
Control	--	--	--	75

Table 6. --Weight gain and crease recovery angle of cotton fabrics impregnated with acidic catalyst (1 percent) and exposed for 24 hours to formaldehyde vapors from methyl formcel

Catalyst	Temperature	Weight gain Initial	Weight gain Fixed	Crease recovery angle-warp
	° C.	Percent	Percent	
$MgCl_2.6H_2O$	50	1.2	0.0	82
	80	2.6	.5	84
$Zn(BF_4)_2.7H_2O$	50	1.3	.0	81
	80	3.4	1.8	130
$CuCl_2.2H_2O$	50	1.6	.4	95
	80	3.2	2.0	141
$Zn(NO_3)_2 \cdot 6H_2O$	50	1.7	.3	81
	80	3.7	2.0	117
NH_4Cl	50	1.9	1.1	147
	80	3.4	2.6	147
Control	--	--	--	75

Table 7. --Wet and dry crease resistance produced by methyl formcel on 1-percent NH_4Cl preimpregnated cotton after various exposure times

Exposure at 80°	Warp crease resistance Wet	Warp crease resistance Dry
Min.	Degree	Degree
15	60	73
30	60	75
60	84	100
120	134	123
240	144	138
480	153	147

with 1-percent ammonium chloride and dried, was exposed to the vapors of methyl formcel at 80° for varying periods of time. By weight gain less than 1-percent formaldehyde was found in the extracted samples. After 120 minutes of exposure, however, the crease resistance, both wet and dry, improved significantly as can be seen from the warp crease angles. The crease recovery angle continued to increase up to 480 minutes of exposure, but the rate of improvement was apparently slowing down.

When samples of the same fabric as used above were exposed to the vapors of methyl formcel and formic acid for 24 hours with no pretreatment being given to the fabric, significant increase in wrinkle resistance was obtained at temperatures in excess of 69° C. as can be seen from table 8. When samples of these formcel-formic acid treated fabrics were cured for 5 minutes at 300° F., immediately upon removal from the reaction chamber, no significant improvement over the uncured samples could be observed from the crease angles. From this data it can be seen that the

Table 8. --Vapor-phase catalyzed reaction of methyl formcel using formic acid as the catalyst

Reaction Temp. (24 hr.)	Warp crease angle Vapor only Wet	Warp crease angle Vapor only Dry	Warp crease angle Post cured Wet	Warp crease angle Post cured Dry
° C.	Degree	Degree	Degree	Degree
30	82	74	94	86
40	94	79	90	87
60	123	98	112	113
80	149	141	143	149

vapor-phase catalyst system resulted in an improvement in the crease resistance.

Table 9 summarizes the results obtained when a series of fabrics were exposed to the vapors of varying amounts of methanol hemiformal (55-percent formaldehyde in methanol) using formic acid as the catalyst while varying the time of exposure and the temperature within the reactor.

Almost equal crease recovery angles both wet and dry were obtained for example with 180 g. of methyl formcel and with 135 g. of methyl formcel as the formaldehyde source with an exposure time of 4 hours at 50° C. Further analysis of the data shows that exposure of samples in the presence of 180 g. of methyl formcel for 24 hours at 80° gave a crease-recovery angle almost identical with that obtained when samples were exposed to 180 g. of methyl formcel for 16 hours at the 80° temperature. The same crease-recovery angles could be obtained with 90 g. of methyl formcel for 16 hours at 80°. Somewhat better wet and dry-crease recovery could be obtained by using 134 g. of methyl formcel for 16 hours at 80°. When tensile strength is considered, the desirability of using the lowest concentration becomes apparent. In general, the tensile strength decreased with increasing time, temperature, and formaldehyde concentration, as well as with increasing crease-recovery angles. In this case, the samples exposed to the vapors from 134 g. methyl formcel for 16 hours at 80° had the highest tensile strengths of the samples with the crease recovery angles greater than 257° (W+F). The data in the table also show that there seems to be a large decrease in flex abrasion at crease recovery angles above 240°; however, the trend in flex abrasion is considerably different than is experienced with conventional pad-dry-cure samples. For the middle values of crease recovery angles, that is between the values of 160° to 240°, the vapor-treated samples consistently showed higher values than those obtained with samples that have been impregnated with formaldehyde by conventional pad-dry-cure techniques. The data confirm that crease angles of 300° are possible, using vapor-phase catalysis of formaldehyde.

A series of samples were prepared by padding with concentrations of methyl formcel from 1/2 to 6 percent in the presence of 1 percent zinc nitrate catalyst (table 10). The samples were frame-dried for 5 minutes at 250° F. and then cured for 5 minutes at 300°, process washed, and redried. It can be seen that the increase in crease-recovery angle from 138° to 199° was accompanied by a 58-percent loss in tensile strength and a 50-percent reduction in flex abrasion at only a 1/2 percent formaldehyde add-on level. At the highest crease recovery angle of 261° (dry), the tensile strength had been reduced by 66.6 percent and the flex abrasion by 79 percent. The tensile losses are greater by pad-dry-cure

Table 9.--Effect of vapor phase formaldehyde concentration, exposure time, and temperature upon the properties of cotton fabrics

Reactor conditions			MCRA (W&F)		Tensile		Stoll flex (2:1/2 lb.)
Methyl formcel	Time	Temp.	Dry	Wet	W	F	Cycles-W
G.	Hr.	°C.			Lb./in.	Lb./in.	
180	4	50	164	179	46	37	397
135	4	50	167	170	51	39	471
90	4	50	155	166	56	35	466
45	4	50	154	162	52	36	484
180	8	50	176	196	51	32	458
180	16	50	200	243	41	26	446
180	4	80	240	257	33	22	362
180	16	80	257	296	22	14	167
180	24	80	262	299	19	14	147
134	16	80	275	304	23	14	144
90	16	80	259	295	21	15	175
45	16	80	264	278	21	15	196

Table 10. --Effect of formaldehyde content upon crease recovery, tensile strength, and flex abrasion (conventional pad-dry-cure techniques)

Percent CH_2O	MCRA (W&F) Dry	MCRA (W&F) Wet	Tensile W	Tensile F	Stoll flex (2:1/2 lb.) cycles-W
			Lb. /in.	Lb. /in.	
None	138	147	60	42	466
0. 5	199	194	25	18	233
1. 0	220	212	24	17	161
2. 0	223	213	26	17	159
4. 0	245	225	20	14	120
6. 0	261	244	20	14	93

treatment than for the vapor-phase treatment shown in table 9. Similarly, the flex abrasion resistance of the pad-dry-cure samples are much lower than for the vapor-phase samples shown in table 9 (about 1/2 for equal crease angles). Figure 1 shows a plot of the data on flex abrasion from tables 9 and 10 versus the wet crease recovery angle. It is apparent that the shape of the abrasion curve for the vapor-phase treated samples are considerably different from the samples that were prepared by pad-dry-cure techniques. Figure 2 shows similar data for flex-abrasion versus dry crease recovery angle. The shape of this curve also is significantly different for the vapor phase than for conventional pad-dry-cure samples. It is believed that these differences result from the crosslinking of the fibers in a less collapsed state where vapor-phase treatment is used than under the curing conditions used in the pad-dry-cure technique. The less collapsed condition results in an improvement in both the tensile strength and the flex-abrasion resistance particularly at the lower crease recovery angles. The flex-abrasion resistance is apparently lost in the vapor-phase treated samples at the higher crease recovery angles due to the increased number of crosslinks.

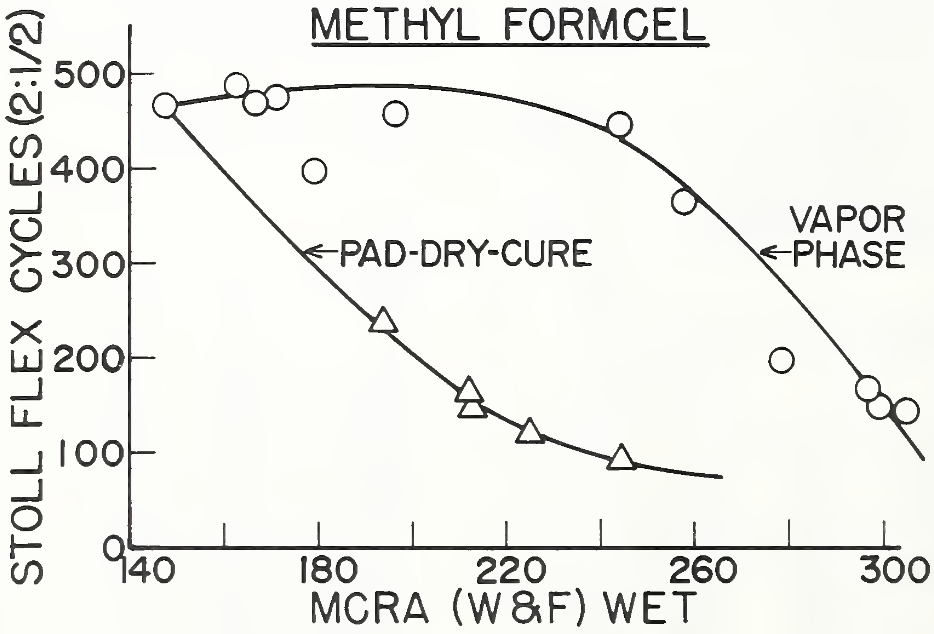

Figure 1.--Plot of the data on flex abrasion versus the wet crease recovery angle.

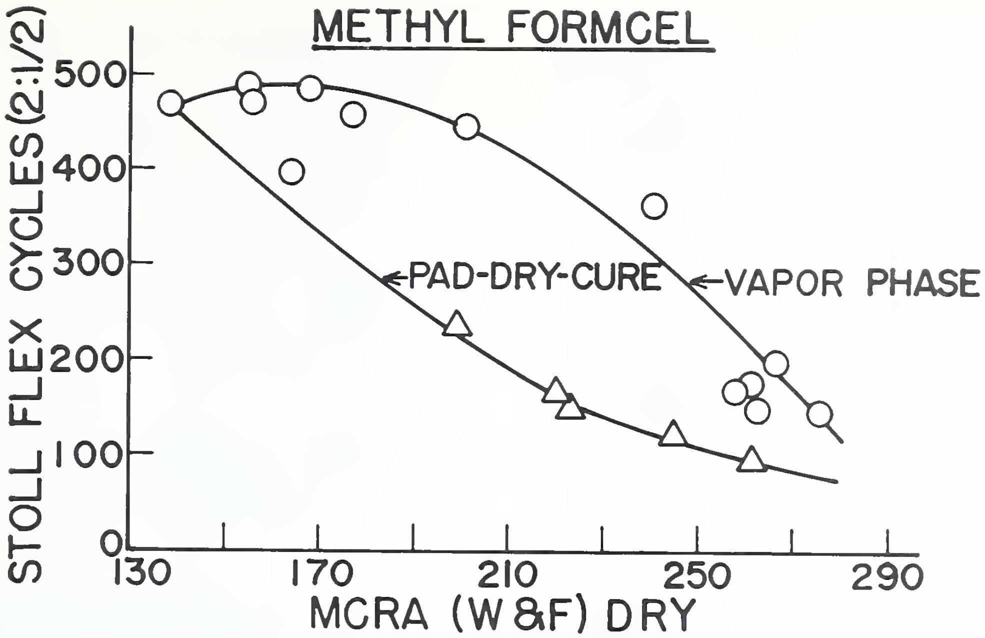

Figure 2.--Plot of the data for flex abrasion versus dry crease recovery angle.

GARMENT TREATMENTS

Cotton brassieres.--Based on the information previously developed from vapor-phase treatments of the 100-percent cotton fabric, a series of tests were made to prepare durable-press 100-percent cotton garments. These tests were intended to demonstrate the practical utility of garment treatments and to test crosslinking uniformity by dyeing tests.

One garment treated was a cotton brassiere. A 5-gallon reactor contained 100 grams of 55-percent methyl formcel and 200 grams of formic acid mixed together and then placed in two separate beakers. The exposure was for 4 hours at 80° C. Both a treated garment and one untreated brassiere were laundered 20 times with a commercial detergent and a hypochlorite bleach at 140° F., followed by tumble drying. The untreated bra had a shrunken, distorted appearance after the first wash. The vapor-phase treated sample, even after 20 repeated washes and dryings, showed no shrinkage, no signs of wear, no rips or tears, and still had a wash-and-wear rating of about 4.5 to 5.0 in various parts.

At the present time, cotton brassieres and girdles cannot be treated by the resin, delayed cure process because the elastic components in the garments cannot tolerate the severe exposure of 10 to 20 minutes at 340 to 360 ° F. The vapor-phase process offers an excellent opportunity to such garment manufacturers to produce durably pressed, washable, cotton, high style undergarments.

Cotton dresses.--Two identical doll-size untreated cotton dresses were purchased. One was exposed for 4 hours at 50° C. to the vapors of methyl formcel-formic acid. When laundered 10 times with detergent at 140° F. and tumble-dried, the untreated garment was badly distorted, expecially in the lace collar portions. The vapor-phase treated garment showed no color or shade changes, no shrinkage, good-shape retention, and a wash-and-wear rating of about 4.0. Of special importance was the fine-shape retention of the cotton lace portions of the dress and the lack of abrasive wear during the washings.

100 percent cotton knitwear.--Two 100 percent boy's cotton knit shirts were obtained.

One was exposed as before. The treated and the untreated shirts were laundered together at 140° F. ten times and tumble-dried. The knit shirt treated by the vapor technique had an excellent appearance after the last wash and was not shrunken. The untreated garment was shrunken and distorted.

100 percent cotton shorts. --Boy's cotton shorts were obtained and treated as above. In this case the vapor-phase treatment produced a shade change in the blue color of the shorts. The dimendional stability and wash-wear performance of the pair of shorts treated by the vapor-phase technique were very good. The untreated garment again was badly shrunken and excessively wrinkled after 10 washes and the last tumble drying.

General comments on cotton garments. --Although the garment treating studies have been few and were confined to small size or miniature single garment treatments, the results have been very encouraging in that some of the previous data on flat fabrics were confirmed with uniformity of treatment in single and multilayers of cotton. Good to excellent wash-and-wear performance and crease retention were obtained with an improved wear resistance over conventional pad-dry-cure resin systems.

VAPOR PHASE CROSSLINKING

Permanent press requirements. --In considering the concept of developing a practical vapor-phase process for treating 100-percent cotton garments and to capitalize on the advantages produced therefrom, it was concluded that for lightweight, soft white cotton items, such as men's shirts, undergarments, knitwear, bed linens, blouses, and related garments, the vapor-phase exposure to methanol hemiformal-formic acid mixture would produce a soft, permanent and completely chlorine-proof finish.

LITERATURE CITED

(1) Anonymous. 1961. A new cotton finish from an old reactant. Textile World 111(12): 109-110.

(2) Arceneaux, R. L., Fujimoto, R. A., Reid, J. D., and Reinhardt, R. M. 1962. Crosslinking of cotton with gaseous formaldehyde. Amer. Dyestuff Rptr. 51: P559-P566.

(3) Chance, L. H., Leonard, E. K., and Reeves, W. A. 1962. The treatment of cotton with formaldehyde in calcium chloride solutions. Textile Res. J. 32: 481-488.

(4) Chance, L. H. Perkins, R. M., and Reeves, W. A., 1961. A process for the modification of cotton with formaldehyde. Textile Res. J. 31: 71.

(5) Compton, J., Martin, W. H., Word, B. H., and Barber, R. P. 1956. The cyanoethylation of cotton. Textile Res. J. 26: 47-66.

(6) Conner, C. J. 1965. Vapor phase reaction of formaldehyde with silicone treated cotton. Amer. Dyestuff Rptr. 54: 618..

(7) Drake, G. L., Jr., Reeves, W. A., and Guthrie, J. D. 1953. Ethylenimine-treated cotton. Textile Res. J. 23: 639-641.

(8) Drake, G. L., Jr., Reeves, W. A., and Perkins, R. M. 1963. Imparting flame resistance to cotton by chemical fixation Amer. Dyestuff Rptr. 52: P608-P611

(9) Fisher, C. H., and Gastrock, E. A. 1956. Administrative document CRPG 245 (5/27/56).

(10) Goldthwait, C. F. 1951. Reaction of formaldehyde with cotton.. Textile Res. J. 21: 55-62.

(11) Greathouse, L. H. 1954. Administrative document CRPG 114 (11/2/54).

(12) Grundfest, I. J., and Gagliardi, D. D. 1948. The modification of cellulose reaction with formaldehyde. Textile Res. J. 18: 643-650.

(13) Guthrie, J. D. 1959. Imparting wet crease resistance to cotton fabrics by crosslinking with aqueous formaldehyde. Textile Res. J. 29: 834-836.

(14) Guthrie, J.D. 1962. Imparting wrinkle resistance to cotton fabrics with vapor from HC1-paraformaldehyde. Amer. Dyestuff Rptr. 51: 507-512.

(15) Guthrie, J.D. 1963. Influence of formaldehyde concentration on the cross-links introduced into cotton cellulose. Textile Res. J. 33: 955-958.

(16) Guthrie, J.D. 1965. Process for treating cellulosic textiles with formaldehyde in vapor form. (U.S. Patent No. 3,180,896) U.S. Patent Office, Off. Gaz. 813: 1380.

(17) Guthrie, J.D. 1964. Process for treating cellulosic textiles with formaldehyde in vapor form. (U.S. Patent No. 3,154,373) U.S. Patent Office, Off. Gaz. 807: 983.

(18) Guthrie, J.D. 1967. Estimation of the length of the oxymethylene bridges introduced into cotton cellulose by formaldehyde and by methylenedisulfuric acid. Textile Res. J. 37: 40-45.

(19) Haydel, C.J., Janssen, H.J., Seal, J.F., Vix, H.L.E., and Gastrock, E.A. 1957. Vapor phase method for preparation of polyacrylonitrile coated cotton yarn and physical properties of the product. Textile Res. J. 27: 957-982.

(20) Janssen, H.J., and Vix, H.L.E. 1956. Administrative document CRPG 244 (6/28/56).

(21) Morton, T.H. 1941. Treatment of cellulosic textile materials. (U.S. Patent No. 2,243,765) U.S. Patent Office, Off. Gaz. 526: 1069.

(22) Negishi, M. 1955. Internal polymerization of vinyl monomers in cotton and regenerated cellulose fibers. Report No. 2 Japan Cotton Tech. Inst., Osaka.

(23) Orr, R.S., Weiss, L.C., Moore, H.B., and Grant, J.N. 1955. Density of modified cottons determined with a gradient column. Textile Res. J. 25: 592-600.

(24) Perkins, R.M., Drake, G.L., Jr., and Reeves, W.A. 1966. Flame-resistant stretch. Textile Inds. 130(1): 125, 127,-129, 164-165.

(25) Reeves, W.A., Perkins, R.M., and Chance, L.H. 1960. Cotton crosslinked at various degrees of fiber swelling. Textile Res. J. 30: 179-192.

(26) Reeves, W.A., Perkins, R.M., and Chance, L.H. 1960. Cotton fabric with wet wrinkle recovery produced without excessive strength loss. Amer. Dyestuff Rptr. 49: 639-644.

(27) Reinhardt, R.M., Fujimoto, R.A., and Arceneaux, R.L. 1966. Process for crosslinking cellulosic textile and paper materials with gaseous formaldehyde. (U.S. Patent N. 3,264,054) U.S. Patent Office, Off. Gaz. 829: 282.

(28) Roff, W.J. 1958. A review of the literature relating to the interaction of cellulose and formaldehyde. J. Textile Inst. 49: T646-T663.

(29) Rowland, S.P., and Post, A.W. 1966. A measure of effective crosslinks in formaldehyde-modified cotton celluloses. J. Appl. Polymer Sci. 10: 1751-1761.

(30) Rowland, S.P., Rollins, M.L., and deGruy, I.V. 1966. Degrees of heterogeneity of distribution of formaldehyde crosslinks in cotton cellulose. J. Appl. Polymer Sci. 10: 1763-1776.

(31) Vix, H.L.E., and Janssen, H.J. 1956. Administrative document CRPG 267 (8/6/56).

(32) Walker, J.F. 1953. Formaldehyde. 2nd Ed., 575 pp., illus. Reinhold, New York.

THE VAPOR-PHASE CROSSLINKING OF PREIMPREGNATED COTTON FABRICS

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Gonzales and Guthrie (4) first investigated the use of gaseous formaldehyde to crosslink cotton which had been preimpregnated with various compounds containing active hydrogens. In general, the mechanical strength properties were retained, or enhanced, and the wet crease-recovery angle improved. Most of this work used paraformaldehyde and HCl dust as the source of reactant and catalyst.

The Gagliardi Research Corporation, under contract to the Southern Utilization Research and Development Division, has expanded upon this earlier work with the view of developing a vapor-phase process for producing durable-press all-cotton products. Besides expanding upon the earlier work, a basic change was made in the reagent-catalyst system.

Methyl formcel, a 55-percent solution of formaldehyde in methanol marketed by the Celanese Corporation, has been employed almost exclusively as the formaldehyde donor and formic acid as the catalyst. This system was found to have advantages over other acid systems including higher reagent concentrations and ease of handling.

Solutions of urea and other water soluble amido compounds produce greater swelling of cotton than does water alone (1, 8, 9). The degree of swelling is greater than that attributable to the specific gravity of the imbibed solutions. Urea solutions impregnated in cellulosic fabrics also increase both the tensile strength and the elongation.

It would be desirable if these effects could be "frozen-in" the cotton fibers by fixing the urea through a vapor phase formaldehyde crosslinking reaction. Aqueous application of formaldehyde is not so effective here, since the dried-in urea would leach out. In the urea preimpregnation, we have in the solid phase cellulose and urea and, in the vapor phase, formaldehyde, methanol, and formic acid. If the urea in the cellulose is accessible to the formaldehyde and catalyst, then formation of the dimethylol urea which reacts with the cellulosic hydroxyls is possible.

Essentially all of the experimentation to be described was conducted in a 5-gallon polyethylene container. The container was equipped with a stirring paddle to provide vapor circulation, a thermometer, and two glass beakers to serve as reservoirs for the methyl formcel and formic acid liquids. Deltapine cotton printcloth was employed. The samples of printcloth, generally 12 by 34 inches were wrapped around a circular stainless steel wire frame (fig. 1) which was then inserted into the polyethylene container. The entire unit was placed inside an oven to conduct reactions at different temperatures.

Uniformity of treatment is generally good, although lower portions of the fabric were somewhat more reacted. This is an engineering problem in circulation to be considered in the upscaling of equipment but did not appreciably influence the laboratory results.

The cotton fabric was padded through a 10-percent urea solution and dried for 5 minutes at 115° C. The fabric was then placed in the reactor at the desired temperature and allowed to react for the desired time. The treated fabric was then washed, conditioned, and tested.

The reaction with formaldehyde is essentially complete during the vapor exposure. Postcuring the treated fabrics for 5 minutes at 150° C. caused only a slight increase in fixed resin yield. Although reaction temperature had definite influence on the weight of formaldehyde absorbed, here too, was little effect on the final weight gain or fixed resin yield.

Examination of some of the results (table 1) on 10-percent urea impregnated cotton treated with methyl formcel-formic acid show that high wet and dry crease resistance are produced by the vapor treatment. The wet values are generally higher than the dry. This is not the common result with normal pad-dry-cure treatments using preformed urea-formaldehyde condensates. While tensile-strength losses appear to be normal for the degree of crease resistance produced, the flex-abrasion resistance is higher than that usually obtained from more conventional

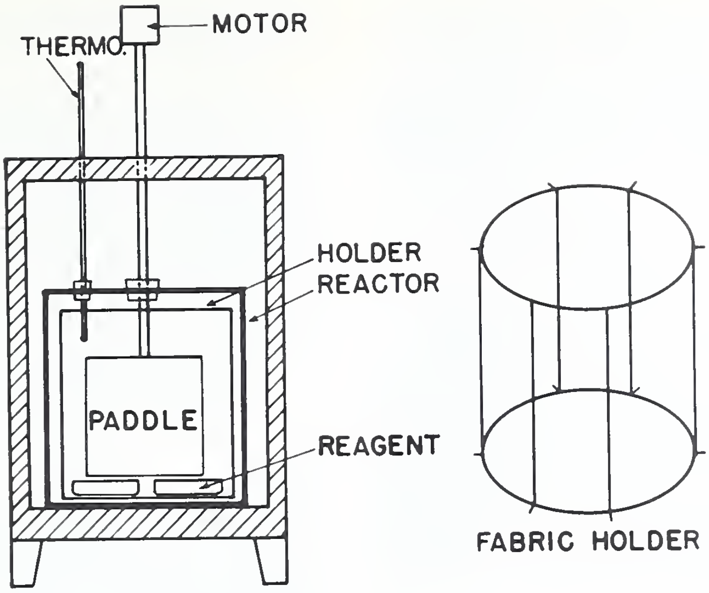

Figure 1.

Table 1. --Effect of methyl formcel-formic acid vapors on urea impregnated cotton

Hours of exposure at 50° C.	MCRA (W&F)		Tensile		Stoll Flex
	Dry	Wet	Warp	Finishing	Cycles-W
			Lb. /in.	Lb. /in.	22 1/2 lb.
Untreated	142	107	64	42	355
10-percent urea:					
2	256	280	37	24	235
4	267	294	36	20	179
8	280	291	33	24	188
24	288	277	31	21	261
5-percent urea:					
24	302	300	31	22	258
20-percent urea:					
24	208	249	53	36	957

approaches (10). The 5-percent urea sample also gave good results. The very high value of flex abrasion reported for the 20-percent urea sample is coincident with an undesirable change in the handle of the fabric.

These data demonstrate that a vapor-phase reaction of formaldehyde with urea-impregnated cotton can be effected by the use of a volatile-acid catalyst. Since the cotton fiber has not been collapsed by any dry-cure step in this process and since it has been pre-swollen with urea, one possible conclusion is that fiber crosslinking is occurring in different regions of the fibers or by different molecular configuration than those normally available in application of preformed methylol urea condensates.

Comparable vapor-phase treatments using hydrogen chloride as the volatile catalyst produce less formaldehyde absorption and a greater dependency of the physical properties on reaction temperature. Samples heated to 80° C. were all too weak for testing.

CYCLIC UREAS AND OTHER REACTANTS

In view of the high crease-resistance values obtained with urea-preimpregnated cottons, the use of selected nonresin forming materials as ethylene urea, ethyl triazone, formamide, ethyl carbamate, and dihydroxyethylene urea were also investigated. These compounds have two or more active hydrogens which can form dimethylol adducts capable of reaction with the cotton cellulose.

Table 2 gives crease angle data for cotton fabrics preimpregnated with different concentrations of some of these compounds, compared with urea. Although the ethylene urea and ethyl carbamate did not perform as well under formic acid catalysis as did urea, it improved wet recovery.

Table 2. --Effect of methyl formcel-formic acid vapors on impregnated cotton (exposure 4 hours at 50° C.)

Nitrogen base in fabric	MCRA (W&F)	
	Wet	Dry
5 percent urea	284	276
10 percent urea	294	267
20 percent urea	188	114
5 percent ethylene urea	258	227
10 percent ethylene urea	261	198
20 percent ethylene urea	264	212
5 percent ethyl carbamate	176	147
10 percent ethyl carbamate	204	151
20 percent ethyl carbamate	193	162

The catalyst was then varied. One percent of ammonium chloride was impregnated into the cotton with the resinous intermediate. Then the dried cotton was exposed to the vapors of methyl formcel only. The urea did not perform well with this catalysis (table 3). Very high wet and dry crease resistance was found with the remaining compounds, especially ethyl carbamate and formamide, in spite of low weight gains.

With hydrogen chloride catalysis, the ethyl carbamate and formamide produced only small weight gains after the first drying step, indicating volatile losses. Further weight loss occurred with these during the vapor phase formaldehyde treatment. The other compounds achieved weight gains comparable to the urea case.

Table 3. --Effect of methyl formcel on cottons preimpregnated with NH_4Cl catalyst

Solution applied	Initial weight gain	Fixed resin postcured	Warp crease-recovery	
			Wet	Dry
	Percent	Percent		
Urea	12.07	6.4	110	99
Ethylene urea	12.38	10.3	151	149
Ethyl carbamate	3.04	1.6	169	148
Formamide	3.28	1.9	155	143
Triazone	12.00	10.0	143	141
Dihydroxyethylene urea	11.50	9.0	143	144

Two nonvolatile carbamic acid esters, hydroxyethyl carbamate and methoxyethyl carbamate, have recently been introduced commercially. When combined with formaldehyde, these esters yield chlorine resistant cotton finishes (5). The Deltapine printcloth was impregnated with a 10-percent solution of hydroxyethyl carbamate and dried 5 minutes at 115° C. The samples were then exposed for 4 hours at 80° C. to various ratios of methyl formcel-formic acid (table 4). Very high wet and dry wrinkle resistance was achieved. The abrasion resistance was good at the intermediate crease angle levels. The 1:4 ratio of methyl formcel-formic acid imparted the greatest reactivity and highest crease angle.

Table 5 compares the effectiveness of methyl formcel and its higher analog, butyl formcel, with formic acid as catalyst in table 5. A continuous flow, 7-gallon reactor, was employed in these studies. The methyl formcel, which has the higher vapor pressure, appears to have behaved more efficiently. In both cases, good properties were obtained. The reaction rate, although slow, appears to have been speeded by use of the continuous reactor design.

Table 4. --Effect of methyl formcel-formic acid vapors on hydroxyethyl carbamate preimpregnated cotton (exposure 4 hours at 80° C.)

Methyl formcel to formic acid ratio	MCRA (W&F) Wet	Dry	Stoll flex warp	Wyzenbeek abrasion warp
Untreated	149	160	670	--
2:1	261	218	599	571
1:1	285	246	322	839
1:2	285	255	275	559
1:4	303	270	264	396

Table 5. --Effect of methyl formcel-formic acid vapors on 10-percent hydroxyethyl-carbamate impregnated cotton

Exposure Time (hr)	MCRA (W&F) Wet	Dry	Stoll flex warp cycles
Untreated	159	122	911
Methyl formcel:			
1-1/2	243	209	731
2	293	248	592
4	299	275	450
Butyl formcel:			
1	220	193	1, 190
2	266	219	810
4	281	247	589

PROPYLENEUREA

Cotton fabrics were impregnated by padding with aqueous 5-percent propyleneurea solutions, framed, and dried. They were then placed in the 5-gallon reactor and exposed to methyl formcel-formic acid vapors for 4 hours at different temperatures. Comparison was made (table 6) with a pad-dry-cure system comprising treatment with dimethylol propylene urea (Fixapret PH and catalyst H7). This fabric was dried and then cured 5 minutes at 150° C. Best results were achieved with the 50° reaction temperature with respect to both crease angles and strength properties. Even the 80° reaction temperature produced a product equal, or a little superior, to the quality of the product prepared by more conventional methods. This repetition of good wrinkle and abrasion resistance appears to be a common phenomenon in crosslinking cotton in a vapor state under mild heat conditions. Indeed, it has been shown by other recent research at SURDD that low-cure temperature of durable-press fabrics increased abrasion resistance with apparent improvement of wet recovery in normal pad-dry-cure treatments. However, one pays for the improvement in properties by a slower reaction rate.

CHLOROSILANE CURING OF RESINS

Vapor-phase chlorosilane reactions on cotton yield a high degree of silicone polymer formation within a few seconds' exposure at room temperature (3). Hydrochloric acid is a byproduct of this reaction. If, then, cotton fabrics are preimpregnated with acid curing types of cellulose crosslinking agents and passed into a reaction chamber containing chlorosilane vapors, then both silicone polymer formation and cellulose crosslinking might occur.

Samples of the cotton fabric were treated with a 10-percent solution of Rhonite R1 and dried 5 minutes at 115° C. The dried fabric, containing 4-percent DMEU, was exposed to vapors of methyl hydrogen dichlorosilane (fig. 2). A strong peak resistance to flex abrasion is observed. The peak is nearly four times higher than the resistance of the control fabric. At longer exposure times and with greater silicone polymer formation, the

Table 6. --Effect of methyl formcel-formic acid vapors on 5-percent propylene urea impregnated cotton

Treatment applied	Time	Temp.	MCRA (W&F) Dry	Wet	Abrasion Stoll	Wyz.	Tensile W	F
	Min.	° C.						
Untreated	-	-	153	141	689	433	58	37
5 percent DMPU	5	150	274	245	345	296	34	23
MFC/HCOOH	240	50	278	259	872	1002	39	27
MFC/HCOOH	240	80	292	280	392	1028	31	22

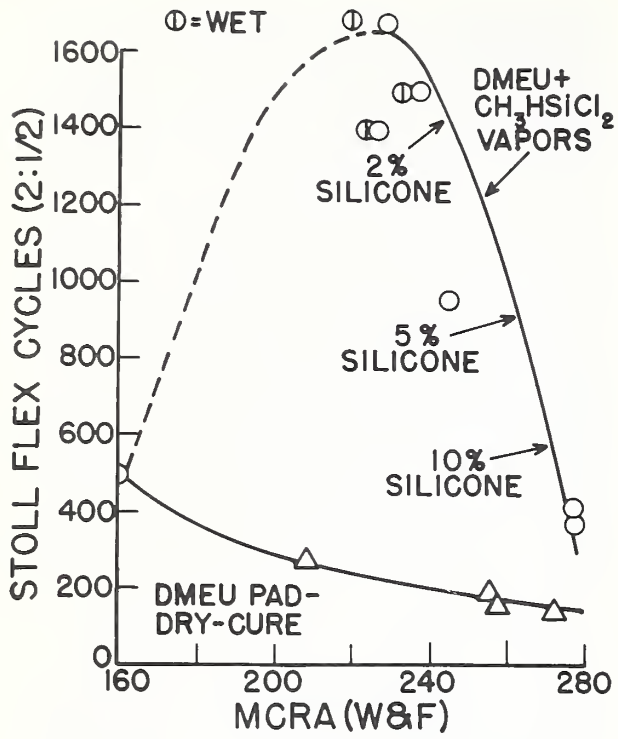

Figure 2.

abrasion curve begins to fall and is back to the level of conventional pad-dry-cure processing in the neighborhood of 300° CRA.

In the experiments previously described, the reactive gases had been removed from the chamber by flushing with nitrogen. In this case, however, the cotton was subject to deterioration through hydrochloric acid attack and the nitrogen flush did not seem suitable. Thus, after another piece of DMEU impregnated fabric had been exposed to chlorosilane vapors, it was removed from the reactor and immediately washed in a 1-percent solution of sodium bicarbonate in isopropanol to neutralize the hydrochloric acid and to deactivate unused chlorosilane. This treatment effected about a 25-percent improvement in the peak resistance to flex abrasion (table 7).

To determine whether simple surface silicone polymer formation was responsible for the improved abrasion resistance, a set of cotton fabrics that had been pretreated with a pad-dry-cure application of DMEU was exposed to chlorosilane vapors. At the same time, additional tests were made by using commercial preformed silicone polymers employed for water repellency (2). The samples contained 7 to 9 percent silicone polymer. While these silicone treatments produced improved flex abrasions showing a maximum peak, the results were not so high as those derived from the chlorosilane vapor treatment providing combined polymer and crosslinking effects. These results again indicate that either the low reaction temperature used in vapor-phase treatment or the location of the polymer in the fibers is influencing the properties. The concentration of water vapor plays an important role in the reactivity of the chlorosilane reaction. The extent of these changes is shown in table 8.

Table 7. --Tensile losses in 4 percent DMEU preimpregnated cotton exposed to methyl hydrogen dichlorosilane

Silane exposure at room temp.	Nitrogen flush 5 min.	Stoll flex cycles warp	Tensile W	Tensile F
			Lb./in.	Lb./in.
Untreated:	No	892	63	45
15 sec.	No	1,755	42	20
60 sec.	No	4,019	37	28
5 min.	No	3,046	35	25
Untreated:	Yes	551	61	46
15 sec.	Yes	1,180	26	21
60 sec.	Yes	393	21	15
5 min.	Yes	542	17	15

An attempt was made to employ methanol hemiformal preimpregnated cotton for exposure to chlorosilane vapor. Hopefully, enough cellulose hemiformal might be formed for subsequent crosslinking by the evolved hydrochloric acid. The cotton fabrics were padded with 20-percent methyl formcel and a very dilute aqueous solution of sodium bicarbonate, then dried 5 minutes at 95° C. They were then quickly exposed to chlorosilane vapors. Little weight gain or wrinkle resistance resulted although appreciable improvement in flex abrasion resistance was noted. It is presumed that, because of the high volatility of the methyl formcel, little remained on the fabric after padding and drying.

HYDROXYETHYLATION GRAFT

Some experiments were undertaken on the vapor-phase hydroxethylation of cotton fabrics

Table 8. --Influence of moisture content on silane grafts of crosslinked cotton fabrics

Sample moisture (initial)	Time	Weight gain	MCRA (W&F) Wet	MCRA (W&F) Dry	Stoll flex cycles-W
Percent	Sec.	Percent			
0 to 1	15	0	227	211	805
0 to 1	300	0	234	224	2,142
4.7	15	.67	162	165	1,875
5.5	300	4.34	244	258	998
10 to 11	15	1.30	255	244	2,735
10 to 11	300	8.76	287	264	370
Pad-dry-cure		-	247	274	324

under various reaction conditions. With high concentration of sodium hydroxide catalyst, 20-percent, and long exposure to ethylene oxide gas, the cotton became water soluble. This solubility occurred at approximately 20-percent ethoxylation. Such high sodium hydroxide concentrations cause gelatinization of the fibers and parchmentizing effects. With 10-percent catalyst, soft nongelatinized fabrics could be obtained. Slight shrinkage occurred under these treatment conditions and both wet crease recovery angle and flex-abrasion resistance were improved. The degree of moisture regain increased in proportion to the degree of ethoxylation. Such improved fiber swelling could perhaps be utilized to advantage in subsequent wrinkleproofing treatments.

Cotton fabrics that had been hydroxyethylated in the vapor state were washed and neutralized with acetic acid. They were subsequently treated by a conventional pad-dry-cure application of 10-percent DMEU. Substantial improvement of resistance to both wrinkling and flexing occurred, particularly with fabrics in the range of 7 to 8 percent ethoxylation. It appears that vapor-phase ethoxylation has considerable promise as a pretreatment to further enhance product quality.

ACRYLATE GRAFTS

Various acrylate monomers, grafted with cotton, produce improvement of wrinkle recovery and abrasion resistance (6). In the contract research, acrylate grafts have been prepared by vapor-phase techniques to modify cotton before crosslinking. Butyl acrylate monomer was grafted to give weight gains of 1 percent to 16 percent. These fabrics were subsequently finished with ethyl triazone by the pad-dry-cure process. They were then dried 5 minutes at 115° C. and cured 5 minutes at 150°. The acrylate grafted samples were difficult to wet out, even with wetting agents. These acrylate grafts also yielded better abrasion and wrinkle resistance properties than is usually found in conventional finishes and are worthy of further study.

SUMMARY AND CONCLUSION

The results obtained indicate the possibility of developing a practical vapor-phase creaseproofing process for treatment of garments. The fabrics could be impregnated in a finishing plant with various formaldehyde reactive compounds, such as propyleneurea, ethyleneurea, and hydroxyethyl carbamate. After reaching the garment plant, the garments would be exposed to vapors of methyl formcel-formic acid. The selection of the impregnation chemical would depend on desired functional properties, durability, weight, cost, and other factors.

Garment Treatment

As an example, cotton twill fabric was impregnated with 10-percent ethyleneurea, dried, and then cut and sewn into miniature pants. The miniature pants were steam pressed and then exposed to the methyl formcel-formic acid vapor system. These pants and an untreated control were laundered 20 times at 140° F. with Tide and tumble-dried after each wash. The treated pants had excellent shape and crease-retention properties after the 20 washes. No signs of wear were evident. The untreated control pants had shrunk and were badly wrinkled.

These garments were later dyed with a direct blue dye. The untreated pants were dyed a uniformly dark navy blue. The treated pants were largely immunized against dyeing. Examination of seams and the multilayers of cloth in the cuffs showed that vapor-phase crosslinking had been apparently uniform throughout the garment.

A preimpregnation vapor-phase technique for 100 percent cotton garments could offer many potential advantages over existing processes. They include ability to operate outside of restrictive precure and postcure patents; higher strength and abrasion resistance; no problems of storage stability; and reaction at lower temperatures to enhance properties and reduce operating costs.

LITERATURE CITED

(1) Chance, L. H., Perkins, R. M., and Reeves, W. A. 1961. A process for the modification of cotton with formaldehyde. Textile Res. J. 31: 71.

(2) Conner, C. J., Reeves, W. A., and Chance, L. H. 1960. New silicone alloy for durable water repellency on cotton. Textile Res. J. 30: 171-178.

(3) Gagliardi, D. D., Jutras, W. T., Jr., Cicione, R. J., and Kenney, V. (In Press) Vapor phase reactions on cotton. Part II: Vapor phase permanent press. Textile Res. J.

(4) Gonzales, E. J., and Guthrie, J. 1965. The crosslinking of cotton cellulose with gaseous formaldehyde in the presence of various compounds. Amer. Dyestuff Rptr. 54: 735, 765-768.

(5) Kullman, R. M. H., Frick, J. G., Jr., Reinhardt, R. M., and Reid, J. D. 1966. Modification of crosslinking effects in cotton fabrics by swelling and methylation. J. Appl. Polymer Sci. 9: 2311-2318.

(6) Prahl, H. F., Tovey, H., and Underwood, C. E. 1966. Short investigation of grafting as a method for improving abrasion resistance of cross-linked cotton. Textile Res. J. 36: 245-250.

(7) Reeves, W. A., Cooper, A. S., Jr., Sloan, W. G., and Harper, R. J., Jr. 1965. All-cotton fabrics for durable press. Textile Indus. 129(10): 74, 75, 77, 79, 82, 85, 86, 88, 103.

(8) Reeves, W. A., Perkins, R. M., and Chance, L. H. 1960. Cotton fabric with wet wrinkle recovery produced with formaldehyde without excessive strength loss. Amer. Dyestuff Rptr. 49: 639-644.

(9) Reeves, W. A., Perkins, R. M., and Chance, L. H. 1960. Cotton crosslinked at various degrees of fiber swelling. Textile Res. J. 30: 179-192.

(10) Tovey, H. 1961. Cotton Quality Study VI. Wrinkle resistance and recovery from deformation. Textile Res. J. 31: 185-252.

THE VP-3 PROCESS--SUMMARY AND CONCLUSIONS

by
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In late 1956, our laboratory developed a vapor-phase process for the chemical bonding of nylon nonwoven fabrics. This process has been in commercial use by one of our industrial clients ever since. In 1957 we also developed, for the same client, a second vapor-phase process for the chemical bonding of polyester nonwoven fabrics. This second process has yet to be used because of the high cost of the gaseous treating agent which is needed and because of its toxicity and flammability.

In 1959 at a meeting of the Metropolitan Section of the American Association of Textile Chemists and Colorists (AATCC), a symposium was held to discuss future technology in textile processing, dyeing, and finishing. In our presentation on the future of textile finishing, we proposed that many existing problems and deficiencies of current pad-dry-cure systems of textile modifications could be solved by the use of pressure reactions, high-temperature steam reactions, solvent-based reactions, and by vapor-phase finishing.

At the 1965 meeting of The Fiber Society, we presented some early data on vapor-phase grafting and crosslinking of cotton fabrics where we showed the value of these in producing stronger cottons and multifunctional finishing effects. At the Fall 1965 Cotton Chemical Finishing Conference, we presented a comprehensive report on the results of basic vapor-phase investigations, which had been obtained under a project sponsored by the USDA. There, we showed further the value of vapor-phase alkylations, esterifications, polymer formations, vapor-phase graftings, and finally, vapor-phase crosslinking in producing improved moisture absorption, oil-repellency, soil-resistance, rot-proofing, and wrinkle-resistance effects with high strength retention in cotton fabrics.

At the 1966 spring meeting of the Textile Research Institute, we first reported on our VP-3 Process concept for producing permanent press 100 percent cotton garments. This process had resulted from our personal practical adaptation of the academic data that we had previously obtained from the broad study of vapor-phase reactions on flat fabrics; specifically, the process involved the use of novel gaseous treating compositions comprising alkanol hemiformals and formic acid. A further potential improvement in our VP-3 Process was presented at the 1966 Cotton Utilization Research Conference in New Orleans under the title of "Vapor Phase Grafting and Its Relation To Permanent Press." Then we showed that the combined vapor-phase pregrafting of cotton with silanic esters, acrylic monomers, and ethylene oxide, followed by vapor-phase crosslinking, produced even better durable press 100 percent cotton garments. Some further work on vapor-phase grafting and crosslinking was presented at the 1966 Cotton Chemical Finishing Conference. Such work was part of a new study being done for the National Cotton Council on cellulose swelling, substitution, and crosslinking wherein vapor phase reactions were used primarily to prove the new concept of cotton crosslinking, internal plasticization, and the influence of swelling.

As can be seen from these recitations, we at GRC have been promoting and studying vapor-phase finishing for over 10 years. We have been trying to get both textile and chemical people on our side to further develop and use such processes. Now, finally, we have at least one commercial organization that has committed itself to invest its own time and a considerable amount of money to reduce vapor phase reactions to a practical state. The first case involves our VP-3 Permanent Press Process which the DHJ Industries of New York has chosen to develop for commercial use. In a second commercial case, we are also trying to perfect a gaseous home-treating process for another client.

Some of the previous speakers have already summarized the earlier basic vapor-phase work on cotton crosslinking, which we have done for the USDA and which they have abstracted from our eight quarterly reports and one final report. Also, we have already recited the various papers describing our VP-3 Process and its advantages over existing resin systems. The results of this process are shown in the various pairs of 100-percent cotton garments on exhibit here. Some of the practical conclusions which we have drawn about our vapor-phase process in its current advanced state of commercial development are the following:

1. The VP-3 Process can be used on 100-percent cotton fine-tailored and regular garments to give durable-press performance not obtainable by conventional resin treatments. This includes higher overall strength and wear resistance and complete durability to multiple launderings with or without chlorine and without yellowing.

2. The VP-3 Process is economical and commercially feasible. By devising special machinery designs and by creating improved gaseous treating systems which adapt the machine to the chemicals and the chemicals to the machine, it has been possible to optimize the results previously obtained in the original primitive laboratory vapor reactors

with regard to chemical consumption, reaction times, and reaction temperatures. Unlike many of the previously reported laboratory curiosities of using refluxing liquids under miniature swatches of cloth, one day to several weeks of exposure, particularly difficult handling conditions, and destruction of the desirable properties of cotton textiles, the improved VP-3 Process is no longer a laboratory curiosity as can be seen in the exhibitied garments treated by the current process.

3. It does not mean, however, that all the practical problems have been solved. Already we have shown that most dyed fabrics produce no shade changes in the VP-3 Process. Some, however, do show slight to major shade changes. Also, the present process is directed to batch-wise operations. We are already working to perfect new continuous garment vapor treating devices using entirely new chemical mixtures and novel mechanical concepts. This work requires new unique chemical engineering developments.

4. Our final conclusion is that because vapor-phase treating devices are going to be commercially available for the VP-3 Process, then continued basic research should be carried out for the other functional chemistry such as soil resistance, water and oil repellency, mildew resistance, absorbency, flameproofing, and other functional effects, which can be done on cotton or cotton blends.

If any of you are not yet acquainted with the principles or chemistry of the original VP-3 Process, I shall be glad to answer any nonconfidential questions and describe the reactor you see here on this platform and in figure 1. I think, probably, most of you have seen this at the Textile Research Institute meeting and at other meetings. For those people who may not have seen it, I will describe the reactor here in detail. You may look at the model later at close hand. Basically, the reactor consists of a closed container. In the main reaction chamber where miniature garments or children's-size garments can be hung is where most of our work on the studying of fabric properties and analytical work was carried out. The main chamber is enclosed in a heating mantle with a temperature control device that controls both the air temperature inside this reactor and also the temperature inside the vapor reagent vessel, which, as you see, is also inside a heating mantle.

Basically, the process is carried out by inserting the textile item in this container, closing the top, and then if conditioning was required, flushing the chamber, either with air or nitrogen, to equilibrate the garments and the atmosphere in the chamber.

We have used nitrogen as a source of the gas carrier simply because it is convenient in the laboratory to operate, but carbon dioxide and other gases, or even air may also be used for particular reagent mixes.

When we have carried out reactions on cotton which required a certain control of temperature, the heating elements were activated. Otherwise, they were not used. In the operation of the reactor, the gas stream goes through the volatile reagent-catalyst mixture. Then it passes into the main reaction chamber in which the garments are hung. By using flow meters, the rate of reagent-catalyst flow around the garments can be controlled.

The valve at the right controls whether the carrier-gas simply flushes the reactor or whether the gas goes through the reactive reagent, where it picks up gaseous molecules from the reagent and carries them into the reactor chamber. From there the excess vapors are exhausted and either thrown away or are simply condensed, collected, reanalyzed, and reused.

When we have used very expensive rare chemicals, such as fluoroacrylates, we have then recovered the excess chemicals from the reactor, distilled them, and reused them in later runs.

On the other hand, when we have used inexpensive chemicals, we have not bothered recovering them. In cases where there was simple reaction, such as with methyl formcel, we simply threw away the excess coming from the exhaust pipe. However, this could be recovered if needed. Some of these operations cannot be done for an industrial reactor which must take into consideration the economics of the whole process, that is, what is the minimum that can be used and how much can be recovered, or is it economical just to

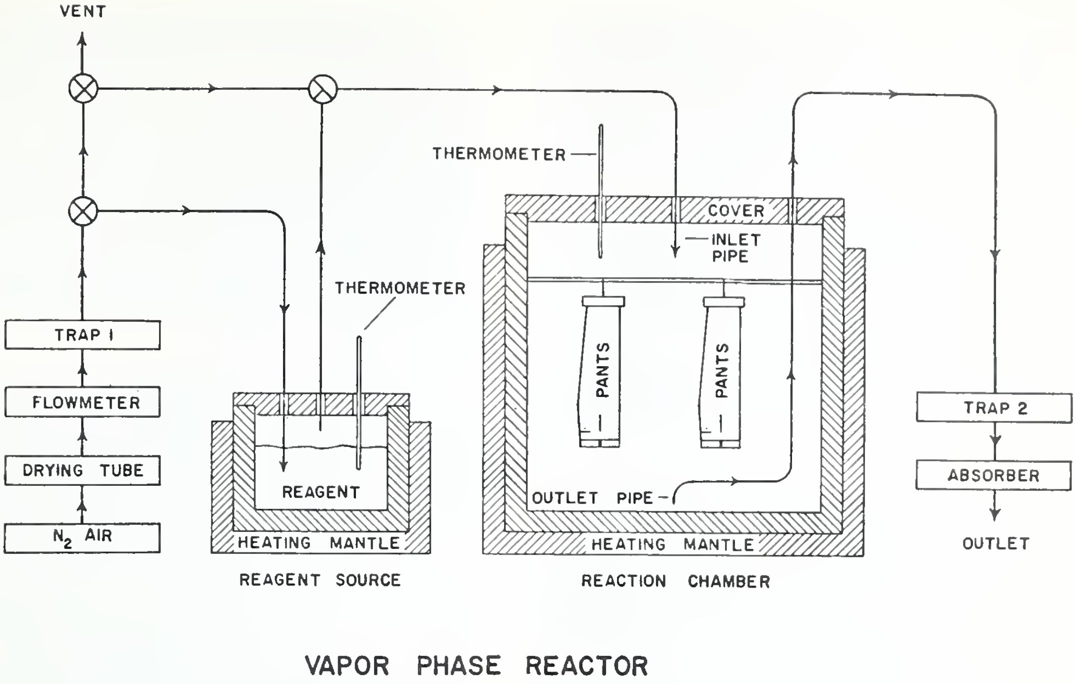

Figure 1.--Vapor Phase Reactor

throw it away? The industrial model now being constructed will help to decide the economics of the VP-3 Process.

Here is a collection of various 100 percent cotton garments which we have treated by the VP-3 Process. These generally contain one untreated sample that has gone through the same number of washings and tumble drying. Note again the shape retention and dimensional stability of these knitted garments and children's blouses. In all of these examples, the 100 percent cotton garment has been treated in a new laboratory reactor without any prior finishing. An alternative procedure, which we have previously described, includes preimpregnation of the cotton with various resin forming materials to produce other effects. Although the emphasis of the VP-3 Process has been on producing high strength 100 percent cotton garments, the same process has been recently tested on polyester-cotton blends and on rayon-cotton blends. Here the improved abrasion resistance has been reflected in eliminating or minimizing the so-called frosting problem in the creases of a pair of trousers. These blue Dacron-cotton pairs of worn cuffs demonstrate the frosting effect and its elimination of the problem by the VP-3 Process. Also, note the appearance of this boy's rayon-cotton shirt after laundering. Note the wide difference in wash-and-wear appearance between the treated and untreated.

As must be quite evident to technical people here in this audience, the translation of a laboratory process to practical commercial utility presents many problems. This includes machinery designs, materials of constructions, explosion hazards, recovery of spent chemicals, control of the reactions, and devising new vapor treating mixtures which will reduce the reaction times and temperatures to the lowest possible level and still achieve the desired performance. It is here, by improved equipment designs and by using new chemical concepts, that we propose to obtain worldwide patent protection on a variety of industrial vapor-phase treating devices, and even on special vapor-phase treating devices for home treatment of garments. Already. from the recent practical development work, we have caused to be filed five new private patent applications on equipment designs and on new vapor-phase treating reagent mixtures for producing durable-press garments and household textiles in a total of 40 countries of the world. No doubt, other private concerns will have their own ideas on other gaseous treating processes and machinery, and will so try to perfect and utilize them in commerce. We hope that all of these activities will benefit the cotton industry.

Before we begin the question and answer period, I want to have you look at the 100 percent cotton shirt which I am wearing. This was produced by the vapor treating process, has gone through many chlorine bleachings and launderings, and has never been ironed. It does not yet show any sign of wear.

I have here other examples of vapor-treated garments. I believe we showed some of these at the Textile Research Institute meeting last spring, but others were recently prepared. We have some knitwear, which has as most of you realize, the great problem of shrinkage control in laundering. These particular knitted shirts have gone through launderings in a home automatic washer. If you place the untreated garment over the vapor-phase treated one, you will note the great degree of dimensional stability which has been produced. Note also the shape retention after tumble drying of the treated article.

Here we have 100-percent cotton little boy's 6-month-old size shirts, one treated and one untreated. Again you can see the durable-press appearance of the VP-3 treated one after laundering.

I think you might be interested in some of the fancy design garments, those untreated versus treated samples after multiple launderings. These lace garments are very difficult things for the technicians in the laboratory to iron, but they were able to do a good job in pressing the garments before they were vapor-phase exposed and then laundered.

For Irving Welch, who is here from American Viscose--I didn't know he was going to be here--we have a special example for rayon: A boy's shirt which was treated by the vapor-phase process and laundered. To make the cotton people here happy, it does contain 45-percent cotton to help it along.

This exhibit again shows the influence of our vapor phase treatment on multiple chlorine washings. I have here one laundered and tumble-dried man's shirt. This happens to be a polyester-cotton DP-shirt costing $7.00 which was bought at a local store in Rhode Island. This shirt has gone through the same number of launderings as these other 100-percent cotton shirts which had been vapor-phase treated. Note the great difference in their appearance after launderings and tumble-dryings.

Here we have an identical test as on this particular shirt which I am wearing. This shirt, which has simply been laundered but never worn by anyone, shows excellent durable press appearance without ironing.

In case any of you men are interested, we have had great difficulty in trying to locate completely untreated cotton men's shirts in Rhode Island. We finally found a supplier who had $1.98 cotton broadcloth shirts which come from Taiwan, Japan, Singapore, or Malaysia. These shirts are excellent when vapor-phase treated.

I think we have also an example of a 100-percent cotton oxford shirt. Unfortunately, this pair is not of the same color, again, because of the difficulty of trying to locate completely untreated cotton garments. Nevertheless, this exhibit shows the effect of laundering. Note the excellent wash-wear appearance of the VP-3 treated shirt compared to the untreated. In this case there was no chlorine used in the laundry. There are certain facets of shirtmaking which I do not understand, but some of the people here in the garment trade were explaining to me earlier the meaning of the improvements in the seams and double-stitch appearance versus the single stitch in the blended cotton example.

I don't know what their terms were, but you can also see the pleat or yoke in the back here which has been stabilized by the vapor phase treatment.

I have here an unusual example of a little girl's Swiss organdy dress with a lace portion here. This was vapor treated. This dress still has its original normal organdy-type feeling and appearance after laundering, whereas the untreated one is now a ball of fabric full of wrinkles.

I think the few examples we have exhibited here do not prove anything by themselves. The important point is that we have been able to confirm (at least to our own satisfaction, and to certain industrial peoples' satisfaction) that vapor-phase finishing can produce improved cotton.

Now, granted we have done no statistical practical testing of hundreds of subjects wearing VP-3 treated shirts, blouses, dresses, pants, and such. The laboratory data and the various laundered garments indicate that we can make stronger durable press-cotton than can be produced by present resin treating methods.

DISCUSSION

Question: Do you have any idea of the amount of investment required for a commercial plant?

Mr. Gagliardi: At the moment, no! We are going to learn by the middle of this year exactly how much the large machine is going to cost. This is currently being designed. At the moment there is no conception of cost, because the chemical engineering problems haven't all been confronted and solved.

Questioner: Mr. Knoepfler mentioned that there was some shade change in using this system on the dyestuffs in fabrics.

Mr. Gagliardi: No, I mentioned that we had tested 40 different dyed and printed cotton fabrics. Up to now, we have found no shade changes except with one particular fabric whose dye composition we don't know.

Questioner: I see. Now, I do notice that on the child's shirt, unless I am not seeing it correctly or the fabric is so puckered it makes a difference, there is a shade difference.

Mr. Gagliardi: Yes, in this tee shirt you will find that the top one looks a little bit bluer, where the bottom one is a little bit yellow-looking.

Questioner: A little bit bluer and a little bit lighter, I think.

Mr. Gagliardi: Yes, as a matter of fact, one of the things that we have found in examining these exposed dyed samples is that we get a great increase in color value. We don't know why this is so, but it has happened in examining commercially dyed fabrics. There is a shade change in here and we think it's to the better as compared with this bottom example. Now, whether it's psychological because of the pucker that you see there, I don't know.

Question: Well, do you know the problems attendant with attempting to use brighteners on resin-treated cottons?

Mr. Gagliardi: Yes. There are many problems that we haven't begun to study as yet. Optical brightness is one of the things that has to be studied as part of the various pretreatments that I mentioned.

Questioner: I can't help mentioning your historical accuracy in your talk, and I am sure you haven't forgotten that the earliest use of gas to treat cotton or linen is approximately 200 years old, when bleaching was done that way with chlorine.

Also, in 1933 there was a machine built in the South, a semicommercial scale machine that treated cotton as a part of the mercerizing process with various chemical vapors to completely change its properties, luster, dyes, and many other things.

I just wonder if there are still much earlier things than you mentioned.

Mr. Gagliardi: If you will read the paper we published 2 years ago, you will find in the preamble a recitation of the history of vapor-phase treatment in the textile industry. They are quite old. In fact, going back even to the formaldehyde system, this really started in 1906 when Eschalier first discovered the reaction between formaldehyde and cellulose or cotton. In the twenties, also, there were many examples from British workers who tried to use acid agers to blow formaldehyde vapors around cloth in a conventional continuous treating system.

Question: Do you mind divulging the dye that you use to determine your crosslinking uniformity?

Mr. Knoepfler: I have that, Don. It's Fastusol Blue LBRRA.

Question: And you say this is diagnostic of whether or not you have a reaction?

Mr. Gagliardi: It's not only diagnostic, it tells you exactly whether you have a crosslinking reaction; the degree of lightness that you obtain can also be directly correlated with the degree of wrinkle resistance that you find in the fabric by mechanical testing.

The purpose of this test--and I wish that people in the textile industry would use it more--is to control production, because if you take light durable-press garments on the market and put them through this kind of test, you find all kinds of areas where there will be blotches of blue dye, whereas in other areas the fabric will be extremely white. This shows poor durable press impregnation, migration, or curing.

Also, this means that there are areas that have been overtreated and areas that have been undertreated, which you cannot see by simply running a wrinkle-resistant test.

Questioner: But this is a direct dyestuff--

Mr. Gagliardi: This is a direct dyestuff.

Questioner: --and I would expect this to react.

Mr. Gagliardi: Let me repeat what happens in this test. If we take untreated cotton and dye it with this dye, the dyeing will produce a very dark navy blue color. When the cotton has been crosslinked, however, such as this collar, it no longer dyes a dark navy blue; that is, the cotton has been immunized against dyeing because of the crosslinkages present in the cellulose.

Questioner: Then you say you get quite a difference. The first gentleman, Dr. Guthrie, mentioned that one possible way to do vapor treatments is to treat the raw cotton and then use that to make your garments.

Mr. Gagliardi: It's a possibility; we are not following that procedure, however.

Questioner: The cotton has quite different dyeing characteristics then.

Mr. Gagliardi: The crosslinked cotton will no longer dye with direct dyes, vat dyes, rapidogens, napthols, or reactive dyes. It is a very simple answer; you cannot postdye crosslinked cotton.

Questioner: It would be very sad.

Mr. Gagliardi: We didn't intend using the VP-3 Process that way. We intend treating garments that have already been dyed in the textile plant.

Question: Did we finish with the dyeing? About 20 years ago, you and Al Nuessle wrote a paper about the relation of toughness and abrasion resistance, and many of us have, over these years, always assumed that toughness had something to do with wear or durability. It seems to me that in the last year or so you have mentioned what I consider a very interesting increase in toughness with this vapor system. Would you mind commenting on that and if you have related this to any kind of durability and wear?

Mr. Gagliardi: We think this is the whole answer, as applied to the particular vapor-phase process of crosslinking cotton. It produces improved tear strength, tensile strength, flex-abrasion resistance, and surface-abrasion resistance as a direct result of improved fiber toughness.

Now, unfortunately, in our laboratories we cannot do single-fiber studies. Therefore, we have not done them; but we have been measuring toughness on fabrics and here we find a direct relation.

Some of the data on toughness was presented at the National Cotton Council last fall where we showed that in every case where there has been an improvement, either by cuff tests on trousers or by flex abrasion, Stoll-flex abrasion, or Wyzenbeek-surface abrasion, the toughness of the fabric was higher than that of the normal resin treated control.

We think this is the whole answer. Now, the reason why the improved toughness comes about may be speculative. We think that the reason we are getting higher toughness in these garments is because: First of all, we are operating at extremely low temperatures; secondly, we are operating on cotton that has never been baked or has never been postbaked; thirdly, we are operating on cotton that is essentially in a swollen state in the systems which we are using.

We believe toughness is really the whole answer as to why better abrasion is resulting. We think that toughness is also the answer to other processes of trying to improve wash-and-wear cotton or durable press cotton from other resin treatments or from the other new system being studied.

Question: Do you experience any problem with release of unreactive formaldehyde absorbed on your fibrous system after treatment with water?

Mr. Gagliardi: In running this particular laboratory reactor with pieces of cloth or small garments, what we have generally done is: After the exposure cycle has been over, we have flushed the reactor anywhere between 5 and 15 minutes to get unreactive gases or we have washed the fabrics.

Then we have followed this by measuring the pH of the cotton and the formaldehyde content of the cloth or both. We have used formaldehyde-reactive materials for flushing and this has indicated that strong air flow is needed to flush out the garment. Washing would be preferred.

However, this is a necessary evil that has to be contended with in this vapor-phase process, because the garment people will probably not be interested in washing garments after they had been exposed in a large-scale reactor. A proper flushing system has to be devised.

Mr. Fortess: The proximity of this gadget overcame my resolve to let cotton have its day in court undiminished by other fibers. I am very much concerned with the fact that most of the testing has involved very gross measurements like Stoll flex or Wyzenbeek or things like that where you are getting numbers, large numbers, but still not turning up the kind of properties that the consumer is concerned with, one of the properties being frosting, the fibrilation properties.

Mr. Gagliardi: There is your frosting problem solved. (Holding up trouser cuffs).

Mr. Fortess: Now, that is wonderful in 100 percent cotton.

Mr. Gagliardi: This happens to be a Fortrel-cotton blend. This is a fabric which you sent to us. (Laughter).

Mr. Fortess: Thank you very much. I was hoping you would say that.

Mr. Gagliardi: Actually, to answer your question more fully, there is a lot more practical testing that has to be done to prove end-use performance. We have been confined, as you know, in a basic laboratory investigation for several years just to study vapor-phase reactions per se.

The question originally was: What could you do to cotton by gaseous treatment? Then, at the latter part of this study we have been trying to adapt some of the information to some practical commercial utilization which could benefit the cotton industry.

The garment people, DHJ Industries--there are representatives here you might want to talk to later--know that they will have to do a lot of practical testing of a large number of garments; they will have to be concerned with many problems, such as sewing thread, zippers, pockets, and colors.

On the other hand, it has been quite surprising to us, that by buying these unknown foreign garments on the market, which I am quite sure were sewn with conventional cotton thread, we have had no problem of seam failure, either by multiple laundering, or, in this one particular example which I have been wearing, by continuous wear.

We have not done any actual measurement of seam strength or any properties of that kind, but in the garments that have been vapor-phase treated, there has been no falling apart of the seams in laundering.

Question: I was wondering, in your looking at various reactants, since you had also looked at HCL and formaldehyde, if you had looked at dichloromethyl ethers?

Mr. Gagliardi: We have evaluated hydrochloric acid, mono- and di-chloromethyl ethers, trifluoroacetic acid, and other acidic reagents. We do not like hydrochloric acid for the very obvious reasons that the fabric falls part. We prefer to find and use, if possible, non HCl sources.

Mr. Shippee: I would like to make a comment rather than a question. It concerns your brief remark on the stitching on the vapor-phase treated shirt you are wearing. I think this represents a very significant achievement and is worthy of further explanation.

It's true, we have all been fighting for the last 25 or 30 years for smoothness of fabric, and more recently, for creases in fabric. These are two very important steps, but when you get all through with this flat piece of fabric, somebody has to make it into a garment, and let me tell you, we still have plenty of problems.

Now, about a year or two ago, there was a development by Cluett for improved seam appearance coupled with permanent press. They found that this improved stitching qualities vary greatly on trouser fabrics. In shirting fabrics, we have not yet found a way to improve the quality of our stitching to the degree we would like.

If any of you have ever looked at your permanent press shirts, you will notice, for example, that all of the seams are put together with a single row of stitching.

This is the type of seams that were used only on the lower quality shirt 10 to 15 years ago. Frankly, these seams perform just as well, but they may not have the fashion appeal that the double-needle stitching had.

Now, since your shirt was a pure-finish shirt, one which was expected to be ironed by the housewife, it was sewn with a double-needle stitching, and the housewife could remove the puckering each time it was ironed.

But with the vapor-phase process, you apparently set the seams in a pucker-free condition and they have not come back during the laundering. This would give us an opportunity, through this process, not only to do a better sewing job as we do it today, but possibly to go back to fashion-type sewing, which may be very desirable.

I think this is a very important step, beyond smoothness and beyond imparting of creases, which could come out of this work.

Mr. Gagliardi: Thank you. I might mention, Mr. Shippee has been a coauthor of some of the papers in this work, because he was involved in the initial program for about a year and a half or so. I think the garment people are the ones who really have to observe, not just what we have done here recently, but what will be done in the future in the larger reactor and to point out these particular garment-constructing problems that we in the laboratory don't get involved with.

Question: Other than solvent extraction, have you any other proof of grafting?

Mr. Gagliardi: In the paper we gave at the Cotton Finishing Conference 2 years ago, we showed the grafting of several acrylic monomers starting with acrylic acid, ethyl acrylate, butyl acrylate, and methyl-methacrylate. We found that weight gain concentrations of up to about 40 percent produced retention of about 100 percent after multiple benzene extractions. In the case of butyl acrylate, ethyl acrylate, and methyl methacrylate, where benzene is a solvent for the homopolymers, we did not get any removal of any matter in those concentration ranges. When, however, the weight gain went over 40 percent--and we had some cases of ethyl acrylate going up to 88 percent in one particular experiment--we found that hot benzene extractions would reduce this weight from 80 percent down to about 40 percent, and then it would reach a level plateau, and on further extraction no more weight loss was observed. Presumably, the residue was grafted.

While this is no direct proof of grafting as everyone knows, we were able to prove, in the case of acrylic acid monomer, which can only form polyacrylic acid (and polyacrylic acid is an extremely water soluble compound) that no weight loss occurred on hot water extractions.

Questioner: My company is Hanes Dye and Finishing. As the Nation's largest producer of pants pocketing material, we would be concerned about the compatability of our formulation with the formulation of other finishes, say, Burlington, Stevens, and so forth, on shell fabrics.

In other words, would it be likely that garment production problems would develop if our formulations were not exactly the same as those of the other fabric producers, or would the role played by the various finishers be so simple as to not cause problems later due to these differences?

Mr. Gagliardi: I think the answer is that there are going to be problems that are bound to come up, but the problems don't have to be there. There are certain basic requirements to this vapor chemistry which are identical to the chemistry that has been used for the last 30 years in resin finishing of cotton and rayon fabrics.

As all of the people here who are involved with finishing or chemical developments know, in order to work most efficiently, as far as chemical combination is concerned, fabrics have to have little or no alkalinity to obtain efficient crosslinking. This has been very well authenticated by a number of papers that have been published on the subject, showing that in fabrics of alkalinity higher than about five hundredths of one percent, you start losing high curing efficiency in any kind of creaseproving or wrinkle-proving treatment.

Secondly, there are other basic requirements which are common to the industry now. These involve the fact that you don't want to put on fabric: yellowing softeners, amine compounds that tend to discolor, either with the heat or light aging or sulfonated oils and fats.

Thirdly, you don't want to put on nitrogenous finishing materials if the garment is intended to be used for a chlorine-resistant application, such as men's shirting, or white dress goods, or anything that is going to be chlorine bleached.

Now, these requirements will have to be kept, that is, you will have to produce fabrics in the finishing plants that will allow these vapor-phase reactions to take place unhindered, but I don't think that they are very different from what is being done now.

Question: You mentioned that the first commercial machine is under design. Could you mention the end product that it is being designed for?

Mr. Gagliardi: I would prefer that you talk to the representative of the DHJ Industries directly, either now or later, I don't know the answer.

Question: Would you have any idea when this machine would be on stream?

Mr. Gagliardi: I don't think I can answer that. I think this is a private matter, and I believe that if you talk to Mr. Nirenberg, who is in the back of the room there, he will probably be glad to tell you.

Mr. Vix: You can see that this has been a very productive contract. There are other areas that we wish we had time to discuss and present.

NATIONAL COTTON COUNCIL OF AMERICA'S VAPOR-PHASE RESEARCH

by
Henry Tovey
National Cotton Council of America
Washington, D. C.

The advantages and disadvantages of vapor-phase processing have already been discussed here. I will not, therefore, spend any time talking broadly about vapor phase, but will rather tell you just what we did and what we found. Actually, none of our projects was specifically on vapor phase. Rather, vapor-phase techniques were used, among others, when we felt that they may offer some special advantages. They were used in two projects which were sponsored by the Council at Bjorksten Research Laboratories, of Madison, Wis. and in two projects at Stanford Research Institute (SRI), in South Pasadena, Calif. The principal investigators at Bjorksten include Helmut Prahl, Chet Underwood, and Fred Hart, and at Stanford Research Institute, Les Berriman, Ron Swidler, and Katherine Wilson.

The Council's first vapor-phase project dates back to March 1963. It was a short, exploratory project, aimed at determining the possibility that the luster of cotton fabrics can be improved by filling in the rugosities on fiber surfaces with a very thin layer of a polymer having the appropriate refractive index. We decided on the vapor phase approach because we thought that polymer deposition from vapor phase may lead to less interfiber and interyarn bonding than deposition from liquid phase.

The standard grafting procedure developed by Bjorksten Research Labs consisted essentially of immersing the fabric sample in the initiator bath, placing it in the reaction vessel, and piping in an inert gas previously bubbled through a pool of the monomer and thus saturated with it.

The initial trials showed that while some monomers could be grafted with nearly all the initiating systems used, others responded to only one or two. A large number of monomers could be grafted--methyl-, ethyl-, and butyl-methacrylate and acrylate, styrene, acrylonitrile, and vinyl chloride, for example--but the add-ons obtained varied with the catalytic system used and monomer type. For example, methyl methacrylate could be grafted to a 95 percent add-on, but the maximum add-on obtained with vinyl chloride was less than 1 percent.

The initial grafted samples from the Bjorksten project didn't show much improvment in luster, and this made us feel that perhaps the surface coating method ought to be augmented by swelling the fiber and maintaining it in the swollen, smooth, and, therefore, light-reflecting condition. This work was performed at Stanford Research Institute. SRI chose the hexamethylene diamine-carbonyl sulfide system which, according to the literature, forms water-white linear polyalkaline urea. Hexamethylene diamine was introduced into fibers by preswelling them with ethylamine, and then substituting hexamethylene diamine for it and removing the residual ethylamine under vacuum. The fabric was cured after exposure to carbonyl sulfide at temperatures ranging up to 125° C. and pressures of a few millimeters of mercury. A polymer was formed. It could not be removed from the fibers by washing in several different solvents; fibers taken from the yarns were permanently swollen, and their cross-sections were more nearly round than those of untreated fibers. However, in spite of the supposed water-whiteness of the polymer, the yarns were amber and the improvement in luster was only slight.

Next SRI tried epichlorohydrin. The idea was to subject caustic-swollen fibers to epichlorohydrin vapors to see whether a graft polymer that would keep them in a highly swollen condition could be formed. The vapor-phase technique at 80° to 90° C. worked, in that epichlorohydrin added to the fabric, but here again the increase in luster was small.

Thus, the Council's initial vapor-phase projects did not lead to a commercial process for improved luster. However, we learned a number of things. First, we learned that monomers from the vapor-phase graft on cotton, perhaps partly on surface but largely internally. Second, we found that it is quite possible to deposit as much as 25 percent of a polymer on or in the cotton fabric without cementing individual fibers together and stiffening fabric hand. Finally, and this is what led us to sponsoring further work involving vapor phase, we found that the treated fabrics generally exhibit increases in both elongation and elasticity, with little change in tensile strength. These findings made us feel that perhaps the grafted fabric may constitute a good substrate for subsequent crosslinking treatments. This reasoning was based on theoretical considerations which were discussed rather extensively at last year's Chemical Finishing Conference. I would like nothing more than to discuss them with you, but they are incidental to the subject of this workshop and I will not take time for them now.

These considerations led the Council to placing another project at Bjorksten Research Labs. The findings of that project were also discussed at last year's Chemical Finishing Conference. As you may remember, it was found that the pregrafting step does in fact mitigate the effect of crosslinking on abrasion resistance, at least as measured by laundering tests--which, incidentally I trust little, but more than I trust instrumental abrasion tests. The best grafts went about three times as long in the washing machine as the conventionally treated cotton. Why some grafts proved better than others we don't know, although there are some indications that the second order transition temperature of the graft, and its potential reactivity with the crosslinking reagent are of importance. I understand that this work, or work similar to it, is continuing at Bjorksten Research Labs under SURDD's sponsorship. I hope that we will hear more about it in the near future.

I will now turn to the last vapor-phase effort on which I will report to you-- a part of a project the Council is currently sponsoring at Stanford Research Institute.

The SRI reaction involves treatment of cotton with formaldehyde in the gaseous state. Of course, we all know that this reaction is as old as the hills, and a lot of effort and money was spent on it. Its basic problem is the loss of strength associated with it, possibly caused by the strong acids which seem to be required to catalyze it. SRI apparently solved this problem by forming the acid catalyst within the fiber and in the exact amount needed. The process consists of subjecting cotton fabric to the action of formaldehyde and sulfur dioxide in the vapor phase. The postulated mechanism of this reaction is that some of the formaldehyde reacts with sulfur dioxide and the regain water in the cotton to give hydroxymethyl sulfonic acid, which is unstable but strong enough to catalyze the formaldehyde-cotton reaction.

The reactor used in the initial studies is a large glass tube, about 8 centimeters in diameter and 40 centimeters in length. It is held in a diagonal position, and at the upper end it has the inlets for the various gases--such as, sulfur dioxide, formaldehyde, water vapor, and air. These gases are allowed to flow over the fabric specimen, which is wrapped around a small frame suspended within the reactor. The gases are vented through a 5 millimeter diameter glass tube at the bottom end of the reactor.

Formaldehyde is generated by heating a suspension of paraformaldehyde in mineral oil. Temperatures between 100° and 140° C. gave flow rates of from 30 to 150 cubic centimeters per minute. Sulfur dioxide is metered from a tank into the reactor at from 5 to 200 cubic centimeters per minute. The reactor and the formaldehyde conduits are kept at about 120° C. with heating tape, but this is apparently not quite sufficient to keep formaldehyde from condensing. I saw quite a bit of the white paraformaldehyde deposit at the edges of the tube. This deposit problem also prevented SRI from using a more accurate formaldehyde metering device.

To date, only investigation of the process variables was possible. Generally speaking, it was found that reaction times as short as 2 to 3 minutes are adequate (table 1). It was found that the concentration of formaldehyde should be kept as high as possible for best results--that is to say, as high as possible within the range tried. It was found that the sulfur dioxide need not be fed in over the entire duration of the reaction--that it can be discontinued after the first minute or two without any change in results. And finally, it was found that the initial moisture content of the fabric appears to be decisive in determining the extent of reaction. This, of course, sounds perfectly reasonable in view of the proposed mechanism of the reaction. The amount of moisture in the fabric would be the limiting factor in the formation of the hydroxymethyl sulfonic acid catalyst, which in turn would determine the extent of reaction between cotton and formaldehyde.

Some of the mechanical properties of fabrics treated in this manner were obtained (table 2).

For untreated printcloth, SRI obtains wrinkle recovery, dry, of about 170° Monsanto, tear strength of 750 grams, and Stoll flex cycles to failure of about 600. Treatment with a typical creaseproofing agent increases wrinkle recovery to about 295°, while tear strength goes down to 400 grams and abrasion resistance to 185 cycles. For a vapor-phase formaldehyde-sulfur dioxide fabric treated to the same wrinkle recovery level of about 300°, tear is 360 grams, and Stoll flex is 270 cycles. This is very much like the conventional treatment. When conventional softeners are included, both the conventional and the vapor-phase treatments also respond similarly, though the Mikon softener seems to do a better job for the conventional than for the formaldehyde treatment.

We then decided to try other materials, and similar experiments were performed using about 30 commercially available lattices, picked on the basis that they form soft films and thus may improve abrasion resistance without stiffening fabric hand too much.

Table 1. --Effect of time in reactor on wrinkle recovery (WR), tear strength, and abrasion resistance

Item	Time in Reactor	WR dry (conditioned)	Tear Strength		Stoll-flex	
	Min.		Pct.	G.	Pct.	Cycles
Untreated twill		130	100	1,620	100	760
Conv. treatment [1]		295	56	900	26	200
Form. + SO_2	5	278	52	850	29	220
Form. + SO_2+7% Rhoplex K14	2	290	94	1,520	220	1,670
Form. + SO_2+7% Rhoplex K14	3	306	72	1,170	146	1,130
Form. + SO_2+7% Rhoplex K14	4	308	64	1,040	140	1,090
Form. + SO_2+7% Rhoplex K14	5	316	56	900	78	590
Form. + SO_2+7% Hycar 2570X15	2	264	90	1,450	207	1,570
Form. + SO_2+7% Hycar 2570X15	3	296	65	1,080	126	
Form. + SO_2+7% Hycar 2570X15	4	310	54	880	133	1,020
Form. + SO_2+7% Hycar 2570X15	5	328	51	840	90	690

[1] Not submitted by SRI -- based on experience with other work.

Table 2. --Wrinkle recovery (WR), tear strength, and abrasion resistance produced by conventional and formaldehyde-SO_2 systems with various additives

Item	WR dry (conditioned)	Tear strength		Stoll-flex	
		Pct.	G.	Pct.	Cycles
Untreated Printcloth	170	100	750	100	600
Conventional	298	53	400	31	185
Formaldehyde-SO_2	300	48	360	45	270
Conv. + Rhoplex K-3	302	72	540	104	620
Form. + SO_2 + Rhoplex K-3	310	63	470	114	680
Conv. + Mikon SF	302	93	700	133	800
Form. + SO_2 + Mikon SF	320	69	520	80	480
Conv. + Rhoplex K-14	328	63	470	61	370
Form. + SO_2 + Rhoplex K-14	318	65	490	230	1,380
Conv. + Rhoplex K-87	328	53	400	85	510
Form. + SO_2 + Rhoplex K-87	312	65	490	208	1,250
Form. + SO_2 + Hycar 2570X15	315	70	530	375	2,250

About 10 of these gave improved flex abrasion or tear strength. These are represented by the data with Rhoplex K-14, K-87, and Hycar 2570 X 15.

As you can see, these are very promising results, but I must warn you--as I keep warning myself--that they are very early, really preliminary, results. I have seen--and I am sure you have too--that the results of preliminary experiments are sometimes difficult to duplicate later on. But even if they should prove reproducible, let us not forget that all we have here is dry wrinkle recovery. I don't know whether the wash-and-wear performance of these fabrics will be as high as one would expect it to be if we dealt with conventional systems. Another important, perhaps overriding, question is whether the improvement in Stoll-flex abrasion will hold in actual wearlife, or even in laundering tests. We all know how easy it is to fool the Stoll-flex machine with a rubbery additive on the fabric.

What I think is fair to say is, first, that the SRI system makes it possible to treat cotton fabrics with formaldehyde to obtain high wrinkle recovery levels at tear strengths and abrasion resistance retentions equal to those produced by conventional treatments. This in itself may be of interest to the industry, in that it may have advantages over conventional processes. What is even more interesting, however, is that it appears that with softeners which have groups capable of reacting with formaldehyde, the vapor-phase treatment produces fabrics which have wrinkle recovery levels of about 300°, tear strength approximately equal to those of the untreated fabric, and Stoll-flex abrasion resistance more than double that of the untreated fabric. The fabrics are not discolored by the treatment, and their hand is good. Obviously, these are very promising results. It seems that this work will take us a long way toward the major objective of cotton research today--toward the development of an all-cotton durable press fabric with high wrinkle resistance, wash-and-wear performance, and fully adequate wearlife.

DISCUSSION

Question: I have a couple of questions. First, is sulfuric acid a catalyst for the reaction or is it necessary to postulate the hydroxymethyl sulfonic acid as a catalyst? Secondly, have you preimpregnated with any other wash-wear resins like Perma-press or any of these things and then treated with SO_2?

Mr. Tovey: I was asked the same question several times during the lunch period. The formation of hydroxymethyl sulfonic acid was postulated by Southern Regional Research Laboratory. Insofar as I know, there is no definite proof that this is the exact mechanism of the reaction. We do know that the moisture content, the regain moisture in the cotton fiber, is the deciding factor in determining the extent of reaction.

Regarding the second question, we did not as yet try any preimpregnation with the exception of preimpregnation or pretreatment with softeners. As you noted, we used several reactive softeners which were padded on the fabric before placing it in the reactor. Of course, and this is something that we are looking forward to with quite a bit of anticipation, we plan to investigate the preimpregnation of cotton with other materials which are capable of reaction with formaldehyde. There are many such compounds. This is one of the things we feel this reaction should be very good for. Using the SO_2 as a catalyst, we hope to obtain results which we couldn't obtain otherwise.

Question: Why are you or SRI working with the particular Rhoplexes that you cited? I don't know whether you know the composition of them, but I happen to know them. These materials have very low glass transition temperature. They are extremely elastomeric materials and even when extremely reacted with high-volatile materials, these still remain extremely tacky.

Now, I notice in the data that tear strength, which is very sensitive to Rhoplex-type material or any acrylic resins with low glass transition temperature, was reported. In this instance, tear strength, flex abrasion, and surface abrasion go up tremendously, but you do not see this effect in practical wear test.

Why is the work being confined to these very soft acrylic resins when, even if you solve all the problems of tensile-strength retention, these resins have extremely high soil-retentive properties?

Mr. Tovey: As you know, the Council policy is to tell everything to everybody who asks, and even to some who don't ask. But this openness can be carried too far; this is why I was a little hesitant of talking about work performed just a couple of weeks ago. You can shoot all kinds of holes in the thing. We don't have wear data. We are nowhere near having wear data on this. The Stoll-flex test is something I don't trust any more than you do. Still, when these same additives were used in both conventional formulations and with the formaldehyde-SO_2 system the improvement in abrasion resistance obtained was much higher for the vapor-phase system. It could be that, for some reasons, the formaldehyde-SO_2 treatment can fool the Stoll-flex test more than the conventional treatment; but this, is all we know so far. The reason we used soft additives is that we felt that soft lattices will have a lesser effect on fabric hand; and, we wanted to avoid stiffening. Several of the materials used also have reactive groups. They were picked because we thought we might be able to hook them on to the fiber through formaldehyde reaction.

Question: I would like to make a recommendation, because I think this thing relates to the work that we have been talking about.

Here you have a formaldehyde reaction. Ours is not quite formaldehyde, even though it has been called that, because we are using an entirely different principle where the alcohol gets reacted in the fiber. In the cases where we have previously reported, we have not been concerned with the presence of such soft elastomeric materials. The improvement in abrasion resistance we have reported has come about solely because of basic changes in fiber properties.

What we would recommend is this: That you study the sulfinic formaldehyde reaction acid in its pristine form without the use of Rhoplexes or any other secondary additive and find out if the improvement in mechanical properties are due to the change in the chemistry of the system and not to this fictitious change that we all find by laboratory testing.

Mr. Tovey: As you may have noticed, the first data I put on the viewgraph was on a treatment with formaldehyde-SO_2 alone. This was compared with a treatment with a conventional agent alone. The second set of data was formaldehyde-SO_2 + Mikon, a conventional polyethylene-type softener. This was compared with a conventional treatment + Mikon. We felt that the results are essentially equivalent. This may be of considerable interest to the industry in itself because, as you pointed out, vapor-phase treatments have advantages over conventional treatments, even if the results are no better than those obtained by conventional treatment. But then we tried to go beyond that, and here we decided to look at two approaches. It is true that you can't improve fabric properties very much unless you improve the fibers, but you can do a little bit by putting things on top of fibers, and this is what we tried first. The second approach is that which I referred to in my reply to our colleague from DuPont. Here we will try to put materials, which are capable of reacting with formaldehyde, inside the fibers before subjecting the fabric to vapor-phase formaldehyde-SO_2.

Question: I noticed most of the work that was done before Gagliardi's work was limited by, I think, a top of about 80° C. Was that correct? Why limit it to 80? Would you have gotten the same kind of results in speed of reaction at 120° that Mr. Tovey got here? Mr. Knoepfler? Dr. Guthrie?

Dr. Guthrie: Well, I wasn't interested in heating at all, because I didn't have any heater in the apparatus, and I didn't want to have to bother about controlling the heat. I used room temperature to keep things as simple as possible.

Mr. Gagliardi: In some of the work that Mr. Knoepfler reported this morning, the experimental data were confined to this reactor which you saw here earlier, to be run for 4 hours at 50° or 4 hours at 80°, because the chemistry at the time the work was done was such that this gave the best balance of tensile, tear, and abrasion properties. The identical reactions, however, were also carried out for 5 minutes at 120° C., such as Mr. Tovey has reported; but, the mechanical properties are much poorer that way and this is why we concentrated on moderating the reactions as much as possible.

PANEL: INDUSTRY'S INTEREST IN THE VAPOR-PHASE TECHNIQUE FOR COTTON FINISHING

M. E. Heard, West Point-Pepperell,
West Point, Ga., Chairman

Comments by
J. W. Weaver
Cone Mills Corp.
Greensboro, N. C.

I am very pleased with the way this meeting turned out. I came in this morning with some misgivings because I wasn't quite sure what we were going to do with the time, but now I am very satisfied with the candid and frank answers that we have gotten from the speakers, particularly Don Gagliardi. While the talks were going on, I was making a list of potential problems that I wanted to bring to your attention. Don has forestalled all these questions by answering them before I could bring them before you.

So let me say again that I am pleased with the tone of the meeting.

I represent a textile manufacturer who supplies fabrics to the apparel trade, and all we have heard so far is what the apparel trade is going to do about vapor-phase finishing.

We have not mentioned anything that the finishers can do in their finishing plants. All I can see out of this whole process is some more problems, such as those we had in durable press.

How can we predict the hand of a fabric when we don't know what's going to happen to it in the apparel manufacturing? How can we predict the shade when we don't know how it's going to be treated in the apparel plant?

Don mentioned that he has tested some 40 or so dyes. I suppose since durable press started out, we must have gone through 400 or 500 dyes, many of which we were forced to reject because we were not sure of their fastness to oven treatment.

Now let me tell you why we, as finishers, might be interested in vapor-phase finishing.

Sometime in the next 20 years I can assure you that we are going to try our best to get away from water-based systems.

Water is getting a little more expensive to get hold of and a lot more expensive to get rid of. All of us are looking and thinking very seriously about solvent systems, solvent scarring, solvent dyeing, solvent sizing, and desizing.

The possibility of doing our finishing in the vapor-phase is certainly a very attractive one, because we would have no residue and no water to dispose of.

Before I came to this meeting, I thought of all the vapor-phase processes that we did, such as acid aging and steaming. After talking to Eric Neale last night, I realized that probably in less than 20 years we are not going to be using those processes, at least as we use them today.

These are all batch processes. If we are going to compete, we have to make it continuous in the same way that we dye and finish.

So I suppose that even the vapor-phase processes that we practice today will be obsolete in a few years.

Comments by
Charles Tomasino
Burlington Industries
Greensboro, N. C.

I find it very difficult to add much else to what has already been expounded this morning, either by the speakers or by Dr. Weaver.

One thing I can add to the discussion is that Burlington has had experience in vapor-phase, not only in the processes mentioned by Dr. Weaver in acid aging and steam aging, but also utilizing the Robbart process described by Don Gagliardi this morning.

One of our divisions pioneered the commercial development of this chlorosilane treatment and has processed millions of yards of fabric. Some of the properties obtained were water repellency, a soft, silky hand, improved resistance to water spotting, and improved luster. These properties were adjudged sufficient to warrant overcoming the processing problems, such as absolute control of fabric moisture, the ability to maintain a constant atmosphere of the atomized or vaporized silanes, efficient utilization of the materials, removal of the by-product which in this case was HCl, and a whole list of other problems such as corrosion resistance of the equipment and uniformity of treatment.

The problem as to whether vapor-phase will be a reality or not can only be determined by a careful analysis of the parameters normally used to assess the feasibility of any process. Whether it will be done by the textile manufacturer or by the garment manufacturer will depend on the end product.

Comments by
J. W. Pearce
United Merchants Research Center
Langley, S. C.

I'd first like to congratulate the investigators that have reported here today on what I consider to be some very interesting work.

The old truism that a problem solved usually creates some multiple number of new problems to be investigated truly insures our continued effort in relation to a gas-phase technique.

I would like to reiterate a plea for a solvent medium consideration. After all, if we remember a little bit of physical chemistry, we realize that the diffusion rate of a gas is an inverse function of the square root of its molecular weight. This may be a rate controlling step in the reaction that we seek from the standpoint of a diffusion mechanism.

You not only have to talk about potentially the diffusion in the gaseous medium, but probably in a liquid medium as well. So it's logical from our point of view to consider the use of controlled solvent species to engage reactions of cellulose.

This offers a reduction, potentially, in the number of, not only diffusion coefficients, but side reactions or controlled degradation reactions of cellulose under rather intense reaction conditions. I would say, objectively, that it might be realistic to compare solvent-phase and gas-phase reactions of cellulose for the more realistic pragmatics of finishing reactions.

Comments by
Werner Pels
Levi Strauss & Co.
San Francisco, Calif.

The reason for inviting us to participate was, I believe, to get some feeling about our reaction to this process and to, perhaps, give some direction to our suppliers. I hope I can do that with some brief comments. Our interest in vapor-phase finishing dates back about 2-1/2 years when we became aware that the Department of Agriculture was sponsoring additional work with Gagliardi Research Corporation on this subject.

At that time, there was already a considerable body of data on crosslinking reactions with gaseous formaldehyde. However, much of the work was still fairly far removed from practicality. So the promise of an expansion of this early work, particularly in the direction of durable-press systems, led us to keep fairly close track with both Gagliardi Research Corporation and the Southern Utilization Research and Development Division.

I must admit that our initial interest in the subject was from the point of view of having at our disposal a better durable-press process--if such a thing exists--than those that we are now using.

If one subscribes to the theory that post-curing produces good results because you are accomplishing setting reactions after garment shaping, then it's not too difficult to extrapolate this line of thinking and speculate on even better results by doing your treatment at the last possible step. In fact, at that time we were engaged in garment treating outside this country. It was an aqueous-phase process, the so-called garment-dipping method.

Our results with this garment treatment process were so encouraging that it was a natural consequence to begin seeking methods that eliminate some of the cumbersome aspects of the dipping technique that we practiced.

This line of thought takes you from aqueous--to solvent--to gaseous-phase processing.

As the vapor-phase work at GRC progressed, some rather interesting data were developed concerning the relationship of crease angle to abrasion resistance. For some values of crease recovery, at least, the ratio was apparently much more favorable than could be obtained from the same reactants in an aqueous system. At this point, the vapor-phase treatment began to hold out a very important promise of better abrasion resistance in durable-press garments. This was an enticing possibility that began to look good for 100 percent cotton. Therefore, what started as a collection of relatively abstract reasons for our interest in vapor-phase garment treatment now became a somewhat more practical matter. This takes us up to the moment. Our interest in vapor-phase garment treatment continues unabated. I must admit that we haven't done much work on our own.

I am sorry that Bob Nirenberg is not a member of the panel. He sounds like the fellow that could really give us the most information on a process which is near commercial feasibility.

With regard to Dr. Weaver's comments, if we ever get to the point where we decide that this, for us, is a feasible thing--and this would be done on the basis of some very basic exploratory work--then there is no doubt that we would stop at that point and enlist whatever aid we could get from our principal suppliers to carry the work to fruition.

It's obvious that this development really can't exist without close cooperation between the garment manufacturer and the suppliers. The same cooperative effort was necessary when we were faced with the introduction of durable press.

DISCUSSION

Questioner: I'm wondering, with due respect to the excellent presentations this morning which dealt largely with vapor-phase treatment, and with the timely comments from the panel of a practical orientation here, whether it's worthwhile getting somebody to summarize what has happened to the excellent work that has been done during the last 2 years using the more classical methods of application, but exploiting such techniques as the wet-curing, swollen-curing, one-phase finishing.

Is anyone willing to say that these have largely failed to meet the needs of 100-percent permanent-press cotton and that we have to look for something completely uniquely different, whether it's solvent-based application or vapor-phase application?

In a sense, I'm throwing out a question to both the speakers this morning and to the panel, because I think it's worthwhile for this group to have an appraisal of what's been done during the last 2 years separate from vapor-phase.

Moderator Heard: Would our panel members like to comment briefly on this question?

Dr. Weaver: If I understood the question, I think it was do we believe that vapor-phase could rescue some of the markets that cotton has lost in the last 2 years? Is that correct?

Questioner: I am thinking more if we have given up some of the approaches that have been tried during the past few years separate from vapor-phase.

Dr. Weaver: We are still trying some of the old approaches. We have not been very successful in reintroducing cotton into some of the markets that it has lost in the last couple of years, for many reasons that I think you are all aware of.

If you want a more optimistic view of this, somebody from the Cotton Council would be much better prepared than I am to answer.

Mr. Tomasino: I'd like to take another approach to this question, from a technical point of view. Technology has to be evolved somehow. As I see it, the vapor-phase is another means of evolving unknown technology. I am sure as the information becomes available, there are people who will find other ways of utilizing it. Therefore, I view the vapor-phase work as adding to the bulk of basic information and perhaps not in itself being a panacea.

Moderator Heard: Dr. Pearce, would you like to add anything to the present state of the art and how we feel about it in industry?

Dr. Pearce: I really don't have anything to add. I thought we were the problems and we are the problem boys to be changed, to be convinced, to accept new and important developments in technology. Based on this precedent, certainly we are going to expect to continue to practice resinations and finishing techniques in light of solving our problems, of being able to accept, digest, and utilize technical advancements as they develop, such as this gas-phase or the solvent treatment.

Moderator Heard: I think the textile industry today is on the move--unfortunately, about 5 or 7 years behind the gray-goods mills. I mean, we screwed the gray-goods mills down real tight a number of years back, and they are producing a quality today at production speeds that they never achieved before.

The finishing plants have put in laboratories and gotten chemists and chemical engineers, and the finishing industry today is very much on the move and very alert.

It is my belief that the day is not too far distant when we will probably have a good wet-fix process for all cotton.

Certainly we have used cotton for many, many years with wonderful satisfaction. We have added other requirements to it as far as the use factor is concerned, but I still believe that these demands can be met.

I don't think we are ever going to replace all the synthetics. Synthetics are here to stay, but, frankly, I think their heyday is probably at its peak right now. I mean that sincerely and I have no pros or cons. I am not wedded to cotton because, I repeat, we run everything and we will run whatever the customer wants. If he wants some asafoetida bound into this yarn, we are certainly going to do it. We will take this yarn and make him a fabric that he can use. I don't know what he will want with it, but if he wants to pay for it, please be assured that we will try to make it for him.

Knowing these three companies and these three gentlemen very well, as well as many other textile companies that are integrated and have their own finishing plants, I can assure you that no stone is being left unturned. Would you gentlemen of the panel agree with me on that? When I say "no stone left unturned," I mean not the slightest pebble, and everything is being looked after in the finishing plant today with the very greatest scrutiny. We are calling in all the suppliers to see if they can make any contributions in addition to our own knowledge and thinking. So, I think with a great deal of soundness, optimistically about the future of finishing, that in the finishing area lies the answer to our cotton problems.

Now, are we the problem boys? Do we just bring another problem, Mr. Anthony, or do you have one now? Is there anybody who would like to fire something at this panel?

Questioner: I would like to ask Mr. Pels how he checks his fabrics or garments before sending them out and whether his tests correlate well with the few returns that we have.

Mr. Pels: I don't know how far to go into that. It depends on what point you are trying to make. Would you tell me what the point is?

Questioner: Well, we hear all these reports about little-boy tests, the knees breaking out.

Mr. Pels: That is a complicated subject that everybody, I suppose, is paying a lot of attention to. It's the subject that induces you to offer your new high tenacity fiber, I suppose. Until we had heard of other garment manufacturers' problems in boys' wear, we weren't really aware of them ourselves. This was primarily because we had not yet marketed the type of garment that produced the initial problems in the industry.

We stopped like everybody else and reexamined our position. We saw that it would be necessary first to initiate service trials that would show us the extent of the problem and then devise laboratory tests to enable us to predict the performance we were going to get with new fabrics. I think we have been fairly successful in both endeavors. We have a better idea now about the performance of all of our garments in those small sizes. We also learned much about the limitations of the laboratory tests that are commonly available to us. To supplement, we have devised our own tests. We are now beginning to market garments that incorporate the durability principles we have learned. In another year we should know whether we have been completely successful in our evaluations.

Questioner: On that same question--I would tend to agree with Dr. Heard that a revolution is likely to take place in finishing technology and controlling finishing, but what we have seen in the permanent press is a transfer of part of the responsibility from the finishing plant to the garment assembly, the cutter. They have done a fairly good job with only part of the responsibility, because the fabrics have been presensitized. Then it's up to the cutter to cut, sew, and properly cure.

Now, with the vapor-phase or the total chemical treatment taking place under the management of the American cutter--and with relatively few exceptions, these are not very technically oriented organizations, nor do they have laboratories or engineers--I am just wondering, not from the point of view of Levi Strauss, who manages this, but what do you think is going to happen to the vapor-phase process where the cutters, in a larger proportion, are going to have to have an even greater responsibility for putting the chemical on as well as curing it and doing all the other things desirable?

Mr. Pels: I really don't know. I have the same reservations that you have expressed. However, I don't know that it's a bigger step to ask a garment cutter to take than the step that has already been taken. You can certainly differentiate between the levels of talent required, but I believe this can be accomplished if the rewards are enticing enough. The important point is not that garment manufacturers have learned to do new things, but that they have expressed a willingness to assume new responsibilities. If willingness and incentive are present, then the rest is simply a matter of acquisition of knowledge in one way or another.

Mr. Shippee: May I add to that, please? I think this is an assumption that somebody is making. I don't recall that there was any basic premise made this morning that vapor-phase was restricted to application by cutters, or even that shirtings is where it would be used. There was reference made to industrial application first being made for shirts, but that could be for shirting fabrics. At the early stage of development where this appears to be, it could be a development for shirting fabrics as well as for shirts. There certainly doesn't seem to be any indication that it would be restricted to the garment treatment.

Secondly, I don't think there is anything really new that we are talking about today. We have given it a new name, "vapor-phase." If we go back 6 or 7 years, we will see that we had gotten pretty tired of reactants and crosslinking agents and we started talking about accessibility. There was a little bit done on swelling phenomena, but the accessibility of the cotton, in general, became popular. My point is that the accessibility studies themselves did not lead to a commercial development. Vapor phase is just one more step along the way after the crosslinking reaction studies. This isn't really anything that is new or different. We just haven't learned how to handle it yet.

Moderator Heard: I certainly agree with your comments on that. This is another tool and another technique. We are adding to the sum total of our knowledge we have found, in an integrated company, that when you do your own finishing, you get corrections made in your gray goods very promptly. If they have to be sold as gray goods somewhere else, it's quite a headache. Frequently, the success--I think my colleagues up here would agree with me--of a particular fabric depends on how you handle it in the finishing plant. The changes that you make in construction to get the ultimate out of the finishing at a price that the customer will pay, takes a very close liaison with the gray goods mill. I am not too concerned about that. I think you are perfectly right that we have a new vista here in this vapor-phase program. If the program shows promise, as it does, and there is opportunity there, please be assured that the companies represented in the textile industry today are not there for philanthropic purposes. They are there to make money, just like the fiber producers are, for their stockholders. If something can be done that will make a product merchantable and usable, and one that will perform, the customers are right on our head for such developments. I don't know which one would get there first, but I'd say we'd all be touching shoulders when we got there. Are there any other questions or comments from the panel?

Questioner: I wonder if you could say something about how these durable-press finishes hold up in laundering, both commercial and in the home.

Moderator Heard: Durable press on all-cotton? Are you speaking of cotton or on synthetics?

Questioner: Well, synthetics mixed with cotton.

Moderator Heard: Well, you get everything, of course, from soup to nuts. I mean, you can go out and buy garments on the market, such as pants--wash them against all-cotton pants and you will come up with about the same thing one time. The next time you will come up with a little bit better results or a little bit worse. Of course, I am in the grandchildren stage now, but I think I am going to have to start a movement to teach all those boys to squat when they shoot marbles, not get on their left knee or their right knee.

There have been many, many problems, you can rest assured. There are many, many problems today: Automation in the cutting plants; laborers complaining; public health looking into it. Where from? Not from cotton, from durable press. There is very little cotton in them, so it's a very live question today. We, as most everybody, have got just a basketful of problems. It's a problem sorting them out and putting a priority on which one has to be solved first. I think the same thing holds true in your respective companies, doesn't it? Which one is the highest; which one has to be handled now?

Questioner: I'd like to ask about the process that was discussed this morning by Mr. Knoepfler where we have a preimpregnation of the fabric with the nitrogenous resin, primarily as a swelling agent where you have a cure in the vapor-phase process discussed by Mr. Gagliardi. The cure is essentially taking place at something like 80° C. How, for example, does the chlorine resistance of this 80° cure compare with chlorine resistance of a fabric cured at the conventional temperatures, conventional pad-dry-cure process?

Mr. Gagliardi: The results are related directly to the type of nitrogen compound which is used to preimpregnate the fabric. If one preimpregnates with urea, you get very poor chlorine resistance. If one preimpregnates with propylene urea, you get chlorine resistance. The purpose of these preimpregnation techniques is directed to certain tactile applications. When one wants a heavy pair of slacks or, for some reason, to increase the weight by 8 to 10 percent, this is the only reason for using preimpregnates.

Now, one point which I never finished discussing this morning was the fact (as you will note on some of the tables which Mr. Janssen was showing on our first process) that where only simple formaldehyde donors were used, the weight gain was small. We related to the history--going back to Dr. Guthrie's personal observations--that very little formaldehyde was needed to obtain a very high degree of wrinkle resistance in cotton.

In our present case of using alkanol hemiformals, we are now involved with higher weight gains of the order of 2 to 3 percent. This is one of the reasons why this shirt has a very lightweight feeling. It's very soft and, in many ways, very silky, although it has no softeners on it. There is no reason to put in urea, propylene urea, starch, or other additives on this particular fabric. There will be other cases where the garment maker wants a particular tactile property and this is the reason why the fabric may have to be loaded with urea, propylene urea, starch, or polyvinyl acetate.

Now, we would not recommend the second type of application except that it is necessary in certain types of garments, for instance, if one needs a firm, heavy, or starch hand on pants materials. Of course, the chlorine resistance will vary with the nature of the preimpregnate. This includes not only propylene urea, but the nature of the softener, the nature of the water repellent, the nature of the acrylic resins, or any other pretreatments. Some of these acrylic resins which were mentioned here are highly chlorine retentive because they have active NH groups in their molecules. This has to be considered if chlorine resistance is desired.

Moderator Heard: There is another question I would like you to answer. Tell us something about the whiteness retention with the formaldehyde vapor-phase. We know little about the formaldehyde vapor-phase treatments compared to conventional treatments on the market today. with paraformaldehyde.

Mr. Gagliardi: Our work was done with kier-boiled and bleached Deltapine cotton fabric which had been specially prepared for us. This was not a mercerized fabric; it was kier-boiled and bleached only. In this particular fabric, without any other pretreatment, there was no change in color or whiteness retention. However, when we got to the stage of buying commercial garments on the market where we did not know what was on the garment except that it was 100 percent cotton, we found a number of cases, for example, where some of the shirts or blouses turned yellow. Then we found that by scouring these materials, when they had a Sanforized label, the yellowing no longer appeared in the vapor treatment. So, as long as the fabric is properly prepared--and I think I touched upon that this morning--if one wants whiteness retention, soil retention, heat resistance, nonyellowing properties, the fabric has to be of such a nature so as not to include discoloring compounds.

Moderator Heard: That was the very point I wanted to bring out--that the finishing industry is really on its toes stretching today in the preparation of goods for every type of treatment of this kind. If these goods are not prepared--and I am not saying this to depreciate any effort that might be made to treat garments--that is exactly the type of thing you will run into and we have encountered it so many times when we didn't know what was on the fabric. I mean, the fabric has to be thoroughly prepared, beautifully prepared to be perfectly accurate, with airtight control of the residual alkaline and free of any softeners or any extraneous compound that might affect your whiteness retention.

MICROSCOPICAL EXAMINATION OF SAMPLES OF COTTON FABRICS GIVEN VAPOR-PHASE TREATMENTS

by
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INTRODUCTION

At the Southern Utilization Research and Development Division, innumerable laboratory samples have been prepared in the course of experiments on the chemical modification of cotton fabrics. With the importance of wash-wear characteristics and the particular emphasis on durable press, the majority of these samples have had some degree of crosslinking. In the comparison of processes, catalysts, crosslinking agents, pretreatments, and post-treatments, microscopical observations have been a useful part of the evaluation analysis, delineating structural features associated with the chemical history of the specimen.

During the past 12 years the microscopical analyses have included occasional samples whose history involved some vapor-phase treatment. In general, the microscopical appearance of fibers from vapor-treated fabrics has been little different from that of samples treated by conventional immersion or padding methods, in fabrics of the same add-on or degree of substitution, except that at low add-ons, homogeneity appears to be somewhat better in samples from the vapor-phase reactions. Maximum add-on achieved by vapor treatment is usually less than by padding methods.

In 1955-56, work on the cyanoethylation of cotton by vapor treatments yielded a series of samples of increasing nitrogen content for which microscopical analysis was requested. Light microscope observations by appropriate staining indicated that uniformity of treatment within the yarns occurred at about a 4 to 5 percent nitrogen level[1] In other experiments involving the vapor coating of cotton fibers with acrylonitrile by an ionic reaction[2], (4) electron microscope observations of surface replicas showed that scoured cotton acquired finer grained and more uniform deposits on the fiber surface than did native, unscoured cotton samples.

By 1961 there was great interest in formaldehyde crosslinking of cotton for crease recovery. Samples from Dr. Guthrie's treatment by fumes from dry paraformaldehyde (3) were submitted for electron microscope observations of cross-sections to determine whether or not crosslinking at room temperature was restricted to the periphery of the fiber. Since that time variously treated samples have been examined microscopically: Those in which the fabric was padded with the fabric was padded with the formaldehyde solution, dried, and subsequently gassed with hydrochloric acid catalyst, and those exposed to vapors of both formaldehyde and hydrogen chloride simultaneously, then neutralized washed, and line-dried. Currently, samples obtained from Gagliardi Research Corporation, representing a vapor-phase carbamate finish, are being examined.

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[1] Conrad, C. M. Internal Memorandum to E.A. Gastrock. January 18, 1956.

[2] Steen, C.J., and Janssen, H.J. The Vapor of Cyanoethylation of Cotton, [Manuscript on file.] 1958.

This paper reports electron microscopical observations of cotton fibers treated by these various vapor-phase methods. Samples chosen for comment in this discussion were selected from the large number available, having roughly the same contents of bound formaldehyde and representing levels of formaldehyde common to vapor treatments (approximately 0. 2 and 0. 5 percent). For comparison, there are included also samples containing similar amounts of bound formaldehyde but which were produced by other than vapor-phase treatments.

MATERIALS

Samples selected for discussion were submitted from the following experimental treatments.

1. Acrylonitrile-coated cotton fibers (Haydel, 4). --A 40-yard skein of 14 s/2 Deltapine cotton yarn was pretreated by immersion for 2 minutes in an aqueous solution of 0. 4 percent potassium persulfate ($K_2S_2O_8$) catalyst and 0. 1 percent Tergitol P-28 wetting agent. It was then centrifuged to 80 percent wet weight content of catalyst. The wetted skein was then mounted in a stainless steel screen tube and placed in a vapor phase reactor. The reactor was evacuated to produce a yarn water content of about 45 percent. Polymerization at 80° C. proceeded by simultaneous emission of acrylonitrile vapors through both tube ends for 10 minutes. Alternate evacuation and air flushing then removed excess acrylonitrile vapors. The polyacrylonitrile skein was removed, washed in water to extract residual nitrile, and dried in a cool air current. The product yielded a nitrogen content of about 5 percent, or about a 19-percent acrylonitrile polymerization.

2. Wrinkle-resistant cotton fabrics from vapor treatment with HCl-paraformaldehyde (Guthrie 3). --Paraformaldehyde dust, containing 0. 9 percent HCl, was generated by placing 20 ml. of concentrated hydrochloric acid in a 50 ml. beaker provided with glass fabric wick on top of 100 g. of commercial paraformaldehyde powder in the bottom of a closed 2 liter widemouthed screwcapped brown bottle for 2 to 4 days. The beaker was removed; bottle closed and shaken well. Standard titrimetric analysis of the dust yielded the percent HCl absorption, indicating partial loose combination of HCl with paraformaldehyde.

The vapor-phase reactor consisted of a cylindrical polyethylene barrel, 32" high by 21. 5" diameter, equipped with a copper paddle wheel driven by variable speed motor, and weighted plexiglass cover. Garments, carefully ironed, were hung by plastic hangers from the cover. Fabric samples were hung from nichrome wires fastened to the cover or taped to the flange overhang of the barrel. (About 100 g. of HCl-paraformaldehyde dust was placed in a 7-1/2 x 1-1/2 inch polyethylene tray on the bottom of reactor barrel). The samples were exposed to the stirred dust for 20 to 30 hours at room temperature; or until test pieces of bleached broadcloth yielded desirable wet and dry hand crumpling results. After completion of each run, the dust was returned to the original screwtop container and regenerated by exposure to HCl acid. Following two or three runs, fresh formaldehyde was used for regeneration, as well. About 15 percent weight loss of dust occurred with each run.

3. Gaseous formaldehyde crosslinking of cotton (Arceneaux 1). --Fabric samples were simultaneously treated with gaseous formaldehyde and gaseous HCl.

The reactor consisted of a 12" by 18" insulated glass battery jar equipped with heating and cooling coils. The slotted top was fitted to hold six samples--frames, stirrer, thermo regulator, thermometer, and two inlet tubes. Sample frames held two 6" by 15" pieces of fabric, spaced by 3/4 of an inch. Gaseous formaldehyde was generated by thermal decomposition of paraformaldehyde at 160° C., utilizing a mineral oil slurry containing 60 g. of paraformaldehyde to 1 liter of mineral oil. The slurry was metered into a preheated mineral oil bath. Formaldehyde vapors were introduced into the reactor one-half hour before the samples. Flow rate was regulated to 250 ml. per hr. for reaction period.

Anhydrous HC1 catalyst, supplied from a commercial cylinder, was connected to the reactor chamber via a flow meter. Flow rate was adjusted to 2. 5 millimoles per minute HC1 addition began immediately after the samples were introduced, and reaction time measured from this point. Variable temperatures of 20 to 80° C. and variable times of 15 minutes to 3 hours were employed. Catalyst concentration varied from 0. 25 percent to 3 percent based on the 72 g. weight of fabric sample. After vapor treatment, the cloth was removed, immediately soaked in 2 percent sodium carbonate and rinsed with water. Washing and tumble drying followed.

4. Preparation of crease resistant fabrics by padding with formaldehyde, drying and then gassing with HC1 (Reinhardt 5). --Samples consisted of cotton cloth which had been scoured, bleached, and desized. These were immersed in 10-percent formaldehyde solution, padded to 100 percent of indicated solution, and dried to a 6- to 10-percent moisture content in a forced draft oven at 60° C. for 7 minutes. The impregnated samples were then exposed to 2 percent HC1 vapors for various time periods of 2 to 30 minutes at 30° in a reactor vessel identical to the one mentioned in the preceding method. The fabric was then washed with H_2O, neutralized in a sodium carbonate solution, machine washed, and dried.

5. Conventional pad, dry, cure treatment [3]. Samples of 80 by 80 fabric were treated with formaldehyde by a pad, dry, cure process with four different catalysts, $MgC1_2$, $Mg(NO_3)_2$ $ZnC1_2$, $Zn(NO_3)_2$. The bath contained 3. 3 percent formaldehyde which was calculated to be the maximum amount of formaldehyde available in a pad bath containing 8 percent DMEU. The samples were padded, dried for 7 minutes at 60°, and cured for 3 minutes at 160° C.

6. Formic acid-formaldehyde treatment.[4] --Cotton was treated in an aqueous solution of formaldehyde containing formic acid as the only catalyst. Differences in bound formaldehyde content in different samples represent differences in time of the sample in the bath.

METHODS

Electron microscopical procedures employed included conventional two-stage replication for surface studies; ultrathin sectioning; and swelling and solution of the thin sections. These specialized techniques have been described in previous publications from this laboratory (6, 7, 8). For clarity these techniques will be briefly described here.

Surface Replicas--Surface topography of fibers can be investigated by a two-stage replication process using polystyrene and carbon successively *8). The fabric to be replicated is placed on a polystyrene-coated glass microscope slide, covered with another slide, and the two slides clamped together. The assembly is heated in an oven at 60° C. for approximately 10 minutes, allowed to cool, and then dismantled. The polystyrene impression is coated with carbon by vacuum evaporation and divided into pieces small enough to be held on electron microscope specimen grids. The polystyrene is dissolved, leaving a carbon replica of the fiber surface which is then shadowed by vacuum evaporation of platinum at a convenient angle (usually 2:1), and then observed with the electron microscope.

Sectioning-- Fiber shapes and the details of internal structure can best be examined by means of ultrathin sections (8). Yarns from the fabrics are carefully untwisted and defibered, and the fibers mixed and parallelized. A small bundle of cotton (approximately 100 fibers combed parallel) is tied at each end with nylon yarn, laid on a glass microscope slide, and coated with a quick-drying nitrocellulose lacquer (Neg-O-Lac) which is allowed to harden. A coating of prepolymerized methacrylate embedding resin is put over the bundle, a coverslip put on, and the slide placed in an oven at 65° C. for 1 to 2 hours. The methacrylate used for this embedding is a 4:1 mixture of methyl and butyl methacrylates containing 1 percent of the catalyst Luperco (CDB) (50 percent 2, 4, -dichlorobenzoyl peroxide in dibutyl phthalate). The slide is cooled, the block of embedded fibers removed from the slide by soaking in water, the coverslip removed with a razor blade, and the embedded block cut to a fine point around the bundle of fibers. Excess methacrylate is trimmed away with a razor blade and the specimen mounted in the vise-chuck of the Porter-Blum microtome. Slices about

[3] Berni, R.J. Confidential Communication. Oct. 1, 1961.

[4] Rowland, S.P. Confidential Communication. Aug. 13, 1965.

600 Å thick are cut with a diamond knife and floated off on a 90/10 water/ethanol solution in the microtome trough. Wrinkled sections are flattened with vapors of xylene. The sections are lifted with a wire loop and placed on carbon-coated specimen grids. The methacrylate embedding resin is removed by placing the grids on filter paper saturated with methyl ethyl ketone, leaving them overnight to soak in these vapors in a closed container. To remove Neg-O-Lac, the grids are then allowed to soak overnight in vapors of chloroform and methyl ethyl ketone in a 50-percent volume mixture. The clean sections are then shadowed by vacuum evaporation of platinum at an angle of 25° to 30° (2:1), examined and photographed with the electron microscope at magnifications of from 3,000 to 27,000 X. In observations of ultrathin sections attention is paid to (1) typical size and shape of section, (2) texture of cellulose within the section, and (3) response of the section to appropriate swelling agents or solvents.

Dissolution of Sections in Cupriethylenediamine Hydroxide ("Cuene").-- *Degrees of crosslinking can be* compared by comparing responses of sections to appropriate solvents (*8*). Specimen grids containing clean sections, freed of embedding resin as described above, are covered with 0.5M cupriethylenediamine hydroxide solution (cuene) for 30 minutes. The sections, washed free of the cuene solution, are shadowed with platinum, as described above, and examined and photographed with the electron microscope. The response of the section to solution in cuene provides a useful method of comparison of crosslinked samples. In general, (there are exceptions), sections that resist solution in cuene have higher crease-recovery angles than those that swell or lose part of their substance by solution. Sections of untreated or scoured cotton dissolve readily, leaving hardly any discernible residues or only masses of amorphous reprecipitated cellulose. In some crosslinked samples, the region near the periphery of the fiber resists the action of cuene, while the core of the fiber dissolves completely, leaving a doughnut shaped residue. In others, the entire section swells tremendously becoming as much as ten times its original diameter without being destroyed; in still others, the section does not change size or shape, but becomes very thin and transparent. In a few samples with very high crease recovery angles, there will be no apparent response of the section at all and its appearance after 30 minutes immersion in cuene will be almost indistinguishable from that of the original section which had not been subjected to cuene. All variations of these phenomena have been observed. In addition to observation of size and shape of the whole section, examination of the texture of the remaining cellulose can be useful. At higher magnifications there are often subtle differences in solidity and texture of the residue which are helpful in comparing one treatment with another. Needless to say, in samples of poor uniformity it is difficult to draw any valid conclusions. In the more uniform treatments, however, comparisons of structural changes can be made with some considerable degree of confidence. It is not to be construed that this technique is a "test" for crosslinking. Samples with good crease recovery angles, but in which the crosslinks can be broken by alkalies, may dissolve readily in the swelling reagent used here. Only in experimental series, where previous history of the samples is well known, can this technique serve as a "test" for crosslinking.

In experimental work, however, it has proved useful in the comparison of individual samples in each given series of experiments.

RESULTS

1. *Acrylonitrile-coated fibers. (Haydel 4).* --*Electron microscope observa*tions of *surface replicas of native and scour*ed cotton fibers vapor coated with acrylonitrile by the method[4] of Haydel and coworkers (*4*) showed that the scoured samples were more uniformly coated with finer grained polymer than the unscoured samples.

2. *Formaldehyde crosslinked samples by the dry cylinder method of Guthrie (3).* -- *When examined by ultrathin sections exposed* to cuene, samples from the vapor-phase experiments of Guthrie (*3*) having bound formaldehyde contents of 0.11 percent, 0.25 percent, and 0.48 percent showed progressively less dissolution. The question originally raised in 1961 about this method of treatment was whether it could be anything but a *surface* reaction. Even in the sample of the *lowest*

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[4] See footnotes 1 and 2.

add-on of formaldehyde, the micrographs show a considerable continuity of the section after exposure to the solvent; but holes in the section are evident. At 0.25 percent HCHO, the effect appeared to be almost the same, but at 0.48 percent HCHO, the section remained intact after 30 minutes' immersion in the rather drastic dispersing agent for cellulose. Some cellulose has been lost, for the section is much thinner, but the material which remains appears to be a continuous web. It is obvious that the reaction is not restricted to the fiber periphery. However, it must be remembered that this particular sample was exposed to the formaldehyde vapors for an extremely long time--30 hours.

3. Vapor-phase crosslinked samples prepared by simultaneous treatment with vapors of HCl and HCHO by the method of Arceneaux (1). --This sample represents a formaldehyde content of only 0.22 percent. It would compare with the Guthrie sample (3) containing 0.25 percent HCHO. Here, however, it would appear from the electron micrograph that the reaction is peripheral. There is more crosslinked material in the outer regions of the fiber than toward the center, implying a diffusion rate dependency at this particular level of treatment.

4. Vapor-phase treatment by gassing with HCl vapors samples previously padded in 10 percent HCHO, dried and cured, by the method of Reinhardt and coworkers (5). --Samples of 0.46 percent HCHO showed reasonable stability to cuene, but there was some disturbance to the section, some swelling, and some loss of cellulose with the development of a few holes. In contrast, the sample containing 0.67 percent bound HCHO showed practically no change in shape or thickness in cuene and was judged to be well crosslinked.

5. Vapor-phase carbamate finish with exposure to a hemiformal (Gagliardi 2). --In a series of samples from a vapor-phase carbamate finish, exposed for different lengths of time to a hemiformal, the effect of time was well illustrated by the electron micrographs of the cross sections.

After 1 hour's exposure, the crosslinking was definitely peripheral with apparently no reaction at the center of the fiber. As time was extended, the reaction evidently became more uniform throughout the section. In those sections of fibers taken from the sample after 3 hours' exposure, the fiber section was little disturbed by cuene. The formaldehyde contents of these samples were not available.

For comparison with the results obtained above on vapor-phase crosslinking treatments, observations were made on samples crosslinked by other than vapor methods, but to the same levels of bound formaldehyde.

6. Formaldehyde crosslinked samples from conventional pad, dry, cure treatments (Berni) . --Cross sections of samples containing 0.2 percent HCHO were compared with those containing 0.4 to 0.5 percent HCHO from samples crosslinked by formaldehyde with different metal salt catalysts in a conventional pad, dry, cure process . The responses of ultrathin sections to solution in cuene indicate differences in the effectiveness of the catalysts. Selected for observation here are those containing 0.2 percent bound formaldehyde, and 0.38 percent bound formaldehyde by analysis of the washed and dried sample. The sample containing the lower percentage of bound formaldehyde was catalyzed by $Mg(NO_3)_2$.

7. Formic acid crosslinking process of Rowland [6] . --Samples of cotton crosslinked by the formic acid process of Rowland to formaldehyde contents of 0.19 and 0.48 percent, respectively, were compared in ultrathin section. The response of the sections to cuene would indicate reasonable good crosslinking in the sample of higher formaldehyde content and practically none in the sample of lower formaldehyde content.

SUMMARY

Electron microscope observations of fibers crosslinked by treatment with formaldehyde by various procedures would indicate that some crosslinking occurs at levels of formaldehyde as low as 0.11 percent and that by vapor-phase techniques fairly good crosslinking is achieved at formaldehyde

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[5] See footnote 3.

[6] Rowland, S.P. Confidential Communication. Aug. 13, 1965.

levels of the order of 0.48 percent. The vapor-phase treatment appears to be diffusion and time dependent. The uniform crosslinking achieved by Guthrie at the 0.48-percent level was the result of approximately 30 hours' exposure.

Samples treated by Arceneaux in vapors of HCl and formaldehyde showed peripheral crosslinking at 0.22 percent HCHO, as did also samples treated with a carbamate finish by exposure to a hemiformal for the first 2 hours of exposure. After 3 hours' exposure, the treatment appeared to be uniform.

LITERATURE CITED

(1) Arceneaux, R. L., Fujimoto, R. A., Reid, J. D., and Reinhardt, R. M. 1962. Crosslinking of cotton with gaseous formaldehyde. Amer. Dyestuff Rptr. 51: P559-566.

(2) Gagliardi, D. D., Jutras, W. J., Jr., and Shippee, F. B. 1966. Vapor phase reactions on cotton. Part I: General considerations and partial results. Textile Res. J.. 36: 169-177.

(3) Guthrie, J. D. 1962. Imparting wrinkle resistance to cotton fabrics with vapor from HCl-paraformaldehyde. Amer. Dyestuff Rptr. 51: 507-512.

(4) Haydel, C. H., Janssen, H. J., Seal, J. F., Vix, H. L. E., and Gastrock, E. A. 1957. Vapor phase method for preparation of polyacrylonitrile coated cotton yarn and physical properties of the product. Textile Res. J. 27: 975-982.

(5) Reinhardt, R. M., Bruno, J. S., Fujimoto, R. A., and Reid, J. D. 1967. Gaseous acid catalysts in the durable press finishing of cottons. Textile Bull. 93(6): 38-41, 67.

(6) Rollins, M. L., Carra, J. H., Gonzales, E. J., and Berni, R. J. 1966. Microscopical comparisons of some reactions of cotton cellulose with ethyleneurea derivatives. Textile Res. J. 36: 185-201.

(7) Rollins, M. L., Moore, A. T., and deGruy, I. V. 1963. Microscopical techniques in finishing research. Amer. Dyestuff Rptr. 52: P479-P488.

(8) Rollins, M. L., Moore, A. T., Goynes, W. R., Carra, J. H., and deGruy, I. V. 1965. Electron microscopy of chemically modified cotton. Amer. Dyestuff Rptr. 54: P512-P524.

DURABLE-PRESS COTTON RESEARCH AT THE SOUTHERN DIVISION

by
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The Southern Utilization Research and Development Division has an extensive research program on durable-press in addition to the vapor-phase work. Actually, the vapor-phase work is about 5 percent of our efforts in this area. I will outline some of the other areas and then comment briefly on some of them. Mr. Rusca will also discuss some of the phases of durable-press research.

(1) A study of the basic priciples involved in modifications that improve abrasion resistance.--Work of this type is done in several of our research groups.

(2) Correlation of test methods with end-use performance.--Just recently Markezich and colleagues showed that there is correlation between the rate of abrasion of a crease in the accelerotor and the rate at which a crease abrades in a trouser cuff when washed and tumbled dried. It takes about one-twelfth as long to carry out this test in an accelerotor as it does in the wash wheel.

(3) Improved crosslinking agents.--Good crosslinking agents are available already, but they are not completely satisfactory. Some will release formaldehyde from a treated fabric during storage or manufacture of the fabric into a garment. Fabrics finished with some agents become discolored. The finish produced by others are not adequately resistant to acids. Some crosslinking agents will meet one or two of these three requirements, but no agent, at least to our knowledge, meets all of these requirements.

A few years ago this Division introduced carbamate crosslinking agents. Methyl and ethyl carbamates were described first. Later hydroxyethyl and isopropyl carbamates were introduced. The crosslinks produced with carbamate finishes take place through methylol groups attached to the same nitrogen atom. Because of the inductive effects associated with the central urethane structure in these compounds, adequate resistance is obtained to alkaline and acidic hydrolysis. Catalysts used with these agents are zinc nitrate, magnesium chloride, and zinc chloride. Some features of finishes produced with carbamates are good durability to laundering, resistance to chlorine bleaching, resistance to acid sours, and resistance to discoloration.

(4) Modification of cotton cellulose with side groups.--This entails modification of the cellulose with small groups such as the methyl group all the way up to modification with graft polymers. This research is aimed at improving abrasion resistance and wrinkle recovery.

(5) New processing techniques.--The vapor phase work is a processing technique which exemplifies this area. Preferential crosslinking which was reported recently is another example. This latter technique puts the crosslinks into selected regions of a fabric such as in one side. Wet or damp curing techniques are also being studied.

(6) Blends of cotton and treated cotton; yarns and fabric structure.--These areas will be discussed later by Mr. Rusca.

(7) Stretch characteristics of fabric and fibers.--Stretch is valuable for improving abrasion resistance whether it is due to the fiber or fabric properties. Both chemical and mechanical techniques are being used to impart the stretch.

(8) Polymers that coat the fibers.--This and the next area will be discussed in some detail below.

(9) Compounds that penetrate the swelled fiber and subsequently polymerize and crosslink the cellulose molecule in the fiber.

Polymers that coat the fibers are useful for improving abrasion resistance and wrinkle recovery. In general, the starting materials for this type of finish are prepolymers. They could be monomers but in the work described here prepolymers were utilized. In some cases these prepolymers are applied from emulsions along with crosslinking agents. In other cases they must be applied from a solvent before applying the crosslinking agent. The prepolymers become crosslinked or extended molecularwise during the heat cure step. Surface polymers can increase recovery of a fabric even without the usual cellulosic crosslinking agent, sometimes up to 270° (W+F). This improvment is equivalent in wrinkle recovery to some good wash-wear fabrics, but the smooth-drying properties are somewhat low in comparison to fabrics having the same wrinkle-recovery angle imparted by the usual agent that crosslinks the cellulose molecules. Therefore, at this stage of the research a combination of crosslinking agents and prepolymers are used to get smooth-drying properties that are needed and to acquire other properties for durable-press goods.

The value of surface polymers can be illustrated with a urethane (Wyandotte Chemical E-406). A 5 ounce, 45° cotton twill treated with 7.2 percent DHDMEU had an initial wrinkle recovery angle (W+F) of 270° which fell to 230° after 50 wash-tumble-dry cycles. The same fabric, which had been treated with 8 percent urethane prior to application of the DHDMEU, had an initial wrinkle-recovery angle of 323° which fell only to 300° after 50 launder cycles. Cured-in-creases were also sharper and remained sharp through the laundering when fabric was pretreated with the urethane. For example, without urethane the initial crease angle was 45° and after 50 launderings it increased to 71°. With urethane and DHDMEU the corresponding angles were 25 and 28, respectively.

A urethane can improve the abrasion resistance of durably pressed trouser cuffs. In this study, cuffs were made from a 63° twill fabric containing 40/2 ply Pima yarn. The fabric used to make some of the cuffs was pretreated with urethane and the other contained only the DHDMEU. In all cases the trouser cuffs were made, pressed to form creases, and then cured. The cuffs were washed and tumbled dried until a failure was observed. Failure is defined as a break in a warp and filling yarn which resulted in a small hole. Without the urethane, cuffs failed at 17 laundry cycles. With the urethane, they went 25 cycles. Initially, the fabric with the urethane was slightly stiffer than the one without it. However, after laundering 30 times, there was no difference in stiffness of the fabrics. The urethane improved the wrinkle recovery significantly (37° W+F). But even with the higher wrinkle-recovery angle, the cuffs containing the urethane were much more resistant to abrasion than fabric without it.

To summarize, when a urethane is used in combination with a conventional crosslinking agent, the wrinkle-recovery angle of treated fabric falls off only slightly during repeated laundry cycles. The creases are sharper initially and remain sharper through laundering. Abrasion resistance as measured by laundering trouser cuffs is improved markedly.

Several other polymer systems improve the various properties of crosslinked cottons, much like that shown above for urethane. Butadieneacrylonitrile latex, acrylates, polyethers, and silicones have given good results. When silicones are used and catalyzed with benzoyl peroxide, no additional catalyst is needed for the N-methylol crosslinking agent.

Polymers that go inside the cotton fiber will be considered next. This is a general approach at SURDD and many other laboratories are studying it. One of the specific approaches we are studying and the one which I want to discuss now is referred to as the poly-set process.

The poly-set method consists of two processing steps. In step 1 fabric is impregnated with a N-methylol type crosslinking agent, a polymerization catalyst, a softener, and other textile modifiers as desired, then dried and cured by using conventional textile processing equipment. The fabric may be washed and dried or processed further without washing.

In step 2 of the process, the fabric resulting from step 1 is impregnated with a crosslinking catalyst, a softener, and with other textile modifiers as desired and dried. At this stage the fabric can either be cured immediately to produce wash-wear or precure durable-press goods, or stored and later made into garments and creased as desired, then cured for the production of creased and shape holding post-cured garments.

The polymerization catalysts suitable for use in step 1 are salts of weak acids and bases. Examples of suitable catalysts are zirconium and zinc acetates. The main purpose of step 1 is to fix the crosslinking agent in the cotton. Some crosslinking agents, such as dimethylol dihydroxy ethyleneurea, can be fixed in the cotton at elevated temperatures by simply acidifying the treating solution with the minimum amount of acid needed to produce a pH of about 4. These weak catalytic conditions are sufficient to promote extensive reaction of N-methylol compounds with amido groups to form polymer but cause only minor reaction between the N-methylol groups and cellulosic hydroxyls. Strong acids are required to catalyze extensive reaction between most N-methylol compounds and cellulosic hydroxyls.

In step 2, the treated fabric from step 1 is impregnated with a conventional catalyst, such as magnesium chloride or zinc nitrate, and cured. The preferred cure temperature appears to be about 160° C. for a few minutes.

The fabrics resulting from step 2 of the poly-set process may contain from about 3 up to about 15 percent of the crosslinking agent. They exhibit a high degree of wrinkle recovery and smooth-drying properties even after many laundry cycles. Stiffness of the fabric, a very important factor in abrasion resistance, is affected by the processing conditions used in steps 1 and 2. Up to about 10 percent polymer can be fixed in a fabric without increasing stiffness much beyond that of the untreated fabric. Abrasion tests by the Stoll-flex method indicate that poly-set fabrics have two to three times the abrasion resistance of conventionally produced durable-press cotton fabrics having comparable wrinkle recovery and smooth-drying properties. Tests made on fibers removed from treated fabrics show that poly-set fibers retain a greater percent breaking strength and elongation-at-break than fibers from conventional durable-press fabrics.

The poly-set process is a flexible technique for producing wash-wear and pre- and post-cure durable-press goods. Most types of N-methylol finishing agents can be used.

There is very little difference in the properties of fabrics whether cured immediately after step 1 or whether the zinc nitrate sensitized fabrics are stored 5 months and then pressed and cured. The abrasion resistance as determined by the Stoll-flex method is much better for the treated samples than for untreated cotton.

Treated fabric made into creased trouser cuffs and evaluated for abrasion resistance by the wash-tumble-dry procedure consistently perform better than similar cuffs treated by conventional resin finishing procedures. Tearing and breaking strength retentions of poly-set treated fabrics are generally about 80 percent and 60 to 65 percent, respectively, of that of untreated control cotton fabrics. Modifying textile finishing agents, such as softeners and polymers that coat fibers, can be added to fabric during step 1 and step 2 processing. Urethanes, silicones, polyethers, and acrylates which have been found to improve abrasion resistance, crease sharpness, wrinkle recovery initially and after repeated laundering, color retention of dyed goods, suppleness and other fabric properties can be used easily in the poly-set process. Fabrics washed after step 1 and impregnated with a cross-linking catalyst release very little formaldehyde or other disagreeable chemicals as determined in the laboratory.

RESEARCH IN THE COTTON MECHANICAL LABORATORY

by
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INTRODUCTION

The Cotton Mechanical Laboratory is concerned with basic research on the effect of fiber properties on yarn and fabric properties and on processing efficiency, the development of new and improved processing equipment, and the development of cotton products to meet old and new end-uses. The laboratory starts with the bale of cotton as it is received at the textile mill and processes the cotton through opening, cleaning, carding, spinning, and weaving into the greige fabric.

This paper briefly discusses two mechanical processing approaches that are producing favorable results.

FABRIC STRUCTURE

Fabrics presently being merchandised in all-cotton durable-press apparel have been designed on the basis of mill experience with fabric structure, and converter and retail experience with consumer demands. While it is generally believed that fabric structure affects the performance of resin-treated fabrics, there appears to have been no research on determining the optimum structure for durable-press fabrics. Some work has been reported on structure suited for wash-wear fabrics.

Two years ago the laboratory set out to investigate the influence of yarn and fabric structure on DP fabric performance, particularly on lightweight fabrics for men's slacks and dress suits. To date the study has been limited to the following:

1. Two yarn numbers--60/2 and 40/2.
2. Two yarn twists--3.0 and 3.75 T.M.
3. Three thread counts in fabric, for both warp and filling.
4. Four weaves: Plain, 45° 3/2 twill (regular), 63° 3/2 twill (steep), and sateen 5-harness.
5. Two weights.
6. One cotton: Pima S-2.

One hundred and forty-four experimental fabrics were produced representing various combinations of the above parameters. The fabrics were given a delayed cure treatment with 18 percent Permafresh 183 to a resin add-on of about 5 percent for the 60/2 fabrics and 6 percent for the 40/2 fabrics.

Samples of the fabrics were pressed flat and cured, and the usual physical properties determined.

The fabrics were evaluated for performance in the washing machine by subjecting four, short-length, cuffed trouser legs, made from each of the 144 experimental fabric structures, to 80 cycles of laundering and tumble-drying, by using the normal cycle for colored goods (cycle B). The number of holes formed in each cuff were noted.

General observations on the performance of these experimental structures are:

1. Mean initial resin add-on:
   60/2 fabrics--5.1 percent
   40/2 fabrics--5.9 percent

   After 80 launderings:
   60/2 fabrics--4.4 percent
   40/2 fabrics--5.3 percent

2. Cuff wash-wear appearance rating (Monsanto plastic replicas):
   60/2 fabrics--4.1 (after 80 launderings)
   40/2 fabrics--4.2

Results in terms of performance in the washing machine:

(a) Weave--45° twills were best with two of the structures showing no damage; following in order were the 63° twills, the sateens, and finally the plain-woven fabrics.

(b) Yarn size--Comparing fabrics of equivalent weight, those woven from the 40/2 yarns wore better than those from the 60/2 yarns, because of the greater mobility of the yarns within the fabric's structure.

(c) Twist--Within the limits of this study, little or no effect on fabric wearability was observed.

(d) Thread count--As thread count increases (either ends or picks), fabric resistance to wear decreases significantly.

The above study was repeated in singles yarn (20/1 and 30/1) with similar results, except that the test cuffs had to be laundered 115 times before all but one of the structures failed, thereby indicating a superiority of singles-yarn performance over ply-yarn performance. The data for this study have not yet been analyzed.

A third study is now underway to determine the effects of yarn and fabric parameters in fabrics in the higher weight range of 8 to 9 oz. per sq. yd.

BLENDS OF UNTREATED AND RESIN-TREATED COTTON FIBERS

The textile industry's practice of blending polyester fibers with cotton fibers to improve the abrasion resistance and strength of durable-press (DP) of fabrics suggested to us that blends of untreated and resin-treated cottons should provide improved performance for DP fabrics.

An investigation of blending resin-treated and untreated cotton fibers was jointly conducted by the Cotton Mechanical Laboratory and the Engineering and Development Laboratory. Without going into detail about the various blend ratios that were used, suffice to say that a 50/50 blend was the best compromise between satisfactory mill processing performance and DP fabric performance. A higher percentage of treated fibers gave better wash-wear appearance, but reduced abrasion resistance and processing efficiency. The reverse was true with a higher percentage of untreated fibers.

The cotton used in this study was 1-1/16" Memphis area growth. It was all scoured and bleached; the blends were made up of scoured and bleached cotton blended with scoured, bleached, dyed, and resin-treated cotton.

Trouser cuffs made from the 50/50 blend in both warp and filling averaged 22 washing and drying cycles before a defect (one or more broken threads) caused by abrasion occurred as compared with 11 cycles for cuffs made from a conventionally resin-treated control fabric, and 6 and 7 cycles for cuffs made from conventionally resin-treated commercial 7-ounce twill and 8-ounce sateen, respectively. Although the trouser cuffs made from the 50/50 percent blend had several minor defects after 40 washing and drying cycles, such as one or more broken threads, they were still serviceable for casual wear.

Further experiments with blends of raw cotton and resin-treated cotton indicate even better abrasion resistance can be achieved.

One major problem remains, however. These fabrics of blended cotton fibers have excess shrinkage in the garment--up to 6 percent in the warp and 2 percent in the filling direction. The laboratory is currently investigating various methods of stabilizing the fabric, such as Sanforizing, compacting, and high-humidity shrinkage.

MACHINERY DEVELOPMENT

Although new textile processing machinery may appear foreign to durable press, the laboratory's machinery research group has recently developed a high-production machine that blends up to 20 bales of cotton. It is of interest for blending resin-treated and untreated cotton, as well as for improving overall operating efficiency of any cotton mill.

Figure 1 illustrates the basic design and operation of the SRRL bale-opener-blender (BOB). Two-inch thick layers from 20 individual bales are placed end-to-end on a conveyor belt. They are stacked in stepped relationship to each other, effectively forming an endless sandwich of layers about 40 feet in length.

The continuous bale is advanced and held against vertical holdback bars. Hooked teeth of counter-rotating processing cylinders pass between the bars extracting tufts as the processing head assembly moves up and down. During operation, the face of the bale is shifted from side to side by pusher plates. This cyclic transverse movement of the bale assures constant production at any desired production rate.

The machine is capable of producing a 20-bale blend of cotton at any production rate from 200 lb. per hr. to a maximum of 1,400 lb. per hr. The tuft weight ranges between 0.2 and 0.5 of a gram at production rates up to 1,000 lb. per hr. This is equivalent to 900 to 2,300 tufts per pound of cotton. At higher rates, tufts may range slightly larger.

Since last July the blender has been undergoing evaluation at Greenwood Mills, Greenwood, S. C. All testing was planned and conducted by the mill staff. Time does not allow discussion of the results, as presented by Leland Beaudrot at the Cotton Research Clinic last week. A few tables will give the highlights of his report. (tables 1, 2, and 3).

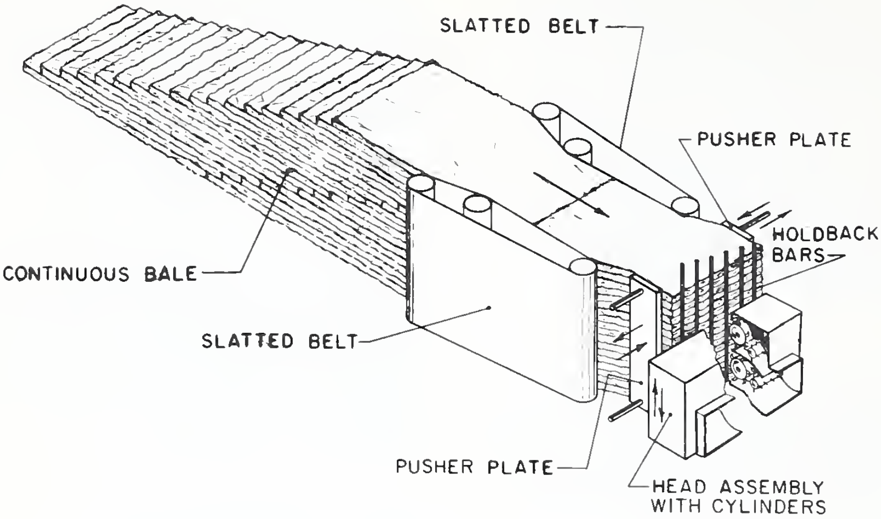

Figure 1---Schematic drawing of bale-opener-blender.

Table 1. --Yarn uniformity

Yarn	Skein Breaking load	 Yarn number	Single strand breaking load	Uster
	Pct. CV	Pct. CV	Pct. CV	Pct. CV
Control, 33/1 Warp	5.24	1.95	10.29	20.30
BOB, 33/1 Warp	4.07	1.52	9.61	20.27
Control, 40.5/1 Filling	6.61	2.15	12.48	20.61
BOB, 40.5/1 Filling	7.15	1.86	11.65	21.95

Table 2. --Fabric strength and quality

	Grab strength	Slub count	Neps	Quality change from control [1/] Yarn	 Weave	 Misc.	 Total
	Lb.	Pt./100 yd.	Pct. free	Pct.	Pct.	Pct.	Pct.
Control	56.9 (warp) 44.7 (filling)	12.2	77	-	-	-	-
BOB	57.9 (warp) 45.6 (filling)	9.8	75	+39	+2	-100	+32

[1/] Based on the joint standards of the Textile Distributors Institute, Inc., and the National Federation of Textiles, Inc.

Table 3.--Fabric quality of additional evaluations

Yarn	Bale blend	Neps	Slub count	Quality change from control[1]			
				Yarn	Weave	Misc.	Total
		Pct. free	Pt./100 yd.	Pct.	Pct.	Pct.	Pct.
		High Production					
Control	43	68	7.7	-	-	-	-
BOB	20	80	4.7	+36	-15	-	+25
		Low Production					
Control	43	64	23.3	-	-	-	-
BOB	20[2]	76	23.3	+16	-	-	+16

[1] Based on the joint standards of the Textile Distributors Institute, Inc., and the National Federation of Textiles, Inc.

[2] Processed through chute-fed card line.

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